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ASPHALT COMPOSITION

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This invention relates to bituminous compositions having improved adhesion characteristics.

The prevention of stripping of asphalt from aggregate is a perennial problem which has received a great amount of attention, especially during recent years. The influence of water on the destruction of asphalt coating has been studied, and various partial solutions have been suggested. The two principal attacks have been to prime the surface of the solid with an agent designed to reduce the stripping action or, secondly, to incorporate an agent in the asphalt to accomplish the same purpose. Combinations of these methods have been attempted with partial success. Acids have been incorporated in the asphalt, and the aggregate has been sprayed with an alkali so that metallic soaps are formed in situ during or after the coating operation. In most cases, however, the soaps which result are dispersible in water or have little or no effect upon the stability of the bituminous composition.

One of the most effective types of additives employed in asphalt comprises various oleophilic high molecular weight amines. These have been used either alone or in conjunction with various oil-soluble acids, such as the higher fatty acids. In certain cases, the latter combination appears to be initially effective. However, due to the formation of amides between the two agents, their cooperative effect substantially diminishes, especially if the asphalt is subjected at any time to heating. Since asphalt is normally shipped from the refinery to a building or road-laying site in heated tank cars, this amide formation constitutes a serious limitation upon the use of this combination of additives.

It is an object of the present invention to provide asphalt compositions having improved adhesion characteristics and exhibiting outstanding anti-stripping properties.

Now, in accordance with the present invention, it has been found that a rigid interfacial film may be formed between a wet aggregate and an asphalt by priming the aggregate with an anion-producing agent and subsequently coating the treated aggregate with an asphalt containing an organic oleophilic basic additive.

Still in accordance with this invention, it has been found that the rigid film so produced causes an unexpected increase in the adhesion of the asphalt to the aggregate. Again in accordance with this invention, the outstanding priming agents have been found to be alkali metal acid salts of a phosphorus acid, while the most satisfactory oleophilic agent is an asphalt-soluble

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amine, especially a polyamine condensation product of acrolein and ammonia, as more fully described hereinafter.

Further in accordance with this invention, it has been found that the resulting compositions have advantageous structural characteristics, such as resistance to disintegration by weather, temperature changes or traffic.

In summary, the present invention primarily comprises the formation of an organic ammonium salt insoluble in either water or asphalt at an asphalt-wet solid interface, resulting in the formation of a rigid interfacial film which increases the adhesion of the asphalt to the solid.

The nature of the rigid film referred to above has not been ascertained, in view of the difficulties attending such an investigation. It is believed that the rigid film consists essentially of a network of crystals of the organic ammonium salt, the interstices of which are filled with a rigidly held film of asphalt. The exact reason for the inflexible nature of the resulting structure has not been determined, but it is believed to be caused by the substantial insolubility of the organic ammonium salt in the asphalt phase as well as in any aqueous phase which may be present.

The nature of rigid films so produced is readily demonstrated by the following technique: A drop of asphalt containing about 1% octadecylamine is dropped into a beaker of water containing an anion-active agent, such as 0.01 molar solution potassium dihydrogen phosphate. A pointed stirring rod is touched against the side of the asphalt drop and then is pulled outwards. The surface of the drop extends to form a pointed projection which remains distorted for a period which may be from about thirty seconds to as much as several days. If the experiment is repeated with asphalt which does not contain the amine, the distortion of the asphalt drop is very temporary in character, the extended portion thereof receding back into the body of the drop within less than one second. A similar result is obtained if the acid phosphate is omitted from the water in which the asphalt drop is placed.

The significance of the rigid film so produced is of practical importance in stabilizing asphalt-aggregate compositions against the deleterious action of water. The advantages to be gained thereby may be determined by the standard asphalt testing methods, several of which are described hereinafter. The rigidity of the interfacial films formed as described above appears

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to be a major factor resisting the stripping action of water. The change in surface spreading pressures of asphalt containing amines is particularly striking when such asphalts are spread as a film on an aqueous surface containing an anion-active agent.

The amines which may be used in accordance with the present invention are those normally found to be partially effective as adhesion agents. These have been fully described throughout the art and include aliphatic amines, particularly those having at least 14 carbon atoms and especially the long-chain primary amines. Secondary and tertiary amines which are oleophilic in character may be used for the present purpose, although primary amines are preferred. Polyamines such as hexamethylene tetramine are especially satisfactory. Two preferred members of this group include amines derived by the ammonolysis of chlorinated paraffin wax, and the polyamine condensation product of acrolein and ammonia. The latter material is especially useful when hydrogenated and reacted with less than an equivalent amount of an organic oleophilic acid, e. g., a fatty acid, such as oleic acid. The amine may be incorporated in the asphalt in minor amounts, e. g., from about 0.25% to about 2%, preferably from about 0.5% to about 1.0%, by weight of the asphalt. However, higher or lower concentrations may also be used in some cases.

The aggregate is to be primed with an anion-producing agent which is soluble in water. The priming may be effected by spraying or otherwise wetting the aggregate. This is conveniently carried out at a mix plant or at the crushing mill, especially when the crushed aggregate is carried away from the grader on a continuous belt, so as to permit a spraying device to be situated above the belt.

The anion-active agent may be any material, either organic or inorganic, which is capable of producing an anion which in turn will form an organic ammonium salt with the amine present in the asphalt. Suitable agents for use in priming the aggregate are phosphates, especially potassium acid phosphate; chromic acid or chromates, especially of weak bases; citric acid and citrates of weak bases; other organic acids such as gallic and tartaric acids; sulfates of weak bases such as ammonium sulfate; alkali metal bicarbonates such as sodium bicarbonate; proteins, such as egg albumen, casein, etc.; nitrates of weak bases such as ammonium nitrate; and organic sulfonates such as the petroleum sulfonates obtained from the so-called "green acids" and the aromatic sulfonates.

The anion-active agent may be applied in the form of a dilute solution. Excellent rigid films are produced by the application of 1-5% (based on the weight of the aggregate) of aqueous solution which is 0.01 to 0.1 molar in anionic content. In the case of a basic aggregate such as limestone, somewhat increased amounts of the priming solution may be necessary for the double purpose of neutralizing the aggregate surface and forming the organic ammonium salt.

The bituminous materials to which the present invention applies especially include pyrogenous asphalts, blown asphalts and the natural asphalts and asphaltites. Other pitches and heavy residues such as wood tar and coal tar derive the same benefit.

The solids which may be treated according

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to the present invention may be plain surfaces such as glass, wood, cement or plaster or preferably may be the standard aggregates employed in the production of asphalt structures such as roads and airport pavings. The method produces rigid films regardless of the character of the aggregate, although superior results appear to be obtained with such aggregates as granite and rhyolite.

It has been found substantially essential to prepare the insoluble rigid films *in situ* as described above. It has been demonstrated that the addition of preformed salts which are substantially insoluble in asphalt or water has only a minor effect on adhesion characteristics. The presence of the rigid films stabilizes the mechanical structure in such a way as to increase the bearing value thereof so as to permit their extended use for strenuous duty, such as in heavy traffic areas.

Especially desirable amines for use in the present invention comprise water-insoluble polyamines obtained by hydrogenating the condensation product of an alpha-beta unsaturated aldehyde and ammonia or an amine. These water-insoluble polyamines may be in the free state or in the form of organic acid salts or in at least partial amide formation with organic acids.

A particularly preferred group of unsaturated aldehydes which may be used in the preparation of these polyamines comprises acrolein and its homologs. Other members of the group are, for example, methacrolein, alpha-ethylacrolein, alpha-propylacrolein, alpha-isopropylacrolein, the alpha-butylacroleins, and their homologs.

Primary amines or, more preferably, liquid ammonia may be condensed with the above types of aldehydes, preferably at a temperature between -70° to about 150° C. In order to improve the stability and color of the resulting products, it is preferred that they be hydrogenated following their preparation. These polyamines are usually viscous oils containing up to about 10% of oxygen. The average molecular weight generally is from about 2½ to about 6 times the molecular weight of the unsaturated aldehyde reactant; hence, the polyamines usually have average molecular weights within the range 135 to about 330. The ratio of the molecular weight to the equivalent weight generally is within the range from about 2.5 to about 4. In order to form a water-insoluble product, these amines may be treated with a higher fatty acid such as oleic acid to form a complex mixture of salts and partial amides. A typical reaction may employ temperatures from about 100° to 300° C. for a period from about five minutes to three hours. Other acids may be used for this purpose, such as naphthenic acids or tall oil.

A typical preparation is as follows:

22 parts of acrolein were mixed with 90 parts of anhydrous liquid ammonia at a temperature of -60° to -70° C. A clear mobile liquid was formed. The excess ammonia was removed from the mixture by allowing the mixture to warm to room temperature in an open vessel. The residue, amounting to 28 parts, was dispersed in 105 parts of absolute ethanol. 5 parts of Raney nickel catalyst were added to the dispersion and the mixture was subjected for one hour to the action of hydrogen gas under a pressure of 1000 pounds per square inch at 100° C. Low boiling material, chiefly ethanol, was removed by distillation under reduced pressure, leaving 18

parts of a viscous, water-soluble oil having the following characteristics:

Molecular weight.....	228.00
Equivalent weight.....	70.00
Per cent carbon.....	61.38
Per cent nitrogen.....	19.25
Per cent hydrogen.....	10.80
Per cent oxygen.....	8.57

The polyamine hydrogenated product thus obtained is water-soluble. In order to insolubilize it, oleic acid is heated therewith at 240° C. for 15 minutes to form mixed reaction products principally consisting of oleic acid salts and amides of the polyamine. Three such products were prepared:

Additive	Equivalent Ratio, polyamine : oleic acid
1A.....	3:1
1B.....	2:1
1C.....	1:1

The following examples illustrate the process of the present invention:

Example I

A soda rhyolite aggregate graded between ½" (100% passing) and ¼" (100% retained) sieves was sprayed with 2% by weight of water. In certain cases, as indicated in the tables below, potassium acid phosphate or chromic acid were present in the water. Six parts by weight of medium curing San Joaquin Valley asphalt was mixed with a hundred parts by weight of the primed aggregate. Prior to mixing with the aggregate, the asphalt had been heated for seven days at a temperature of 120° C. As noted in the examples which follow, various amines were present in some of the asphalts employed. The coated aggregates were allowed to stand in the open air at about room temperature for one hour after which they were covered with distilled water for twenty hours at room temperature. The percentage of the aggregate surfaces still coated with asphalt after this treatment was then estimated. In the first case, an acrolein-ammonia condensation product, which as hydrogenated and in an amide formation with one-third of an equivalent weight of oleic acid, was employed as the asphalt additive. The results obtained are given in the following table:

Percent Polyamine in Asphalt	Priming Solution	Percent Coating Retained
1.0.....	Water.....	25
None.....	0.05 M KH ₂ PO ₄	10
1.0.....	0.05 M KH ₂ PO ₄	65
1.0.....	0.1 M KH ₂ PO ₄	75

Example II

The above test was carried out as described, using C₁₆-C₁₈ substantially straight-chain amines as the asphalt additive. The results obtained are given in the following table:

Percent Amine in Asphalt	Priming Solution	Percent Coating Retained
0.75.....	Water.....	30
None.....	0.05 M CrO ₃	10
0.75.....	0.05 M CrO ₃	80

I claim as my invention:

1. An asphalt composition comprising as its predominant ingredients an asphalt, a wet ag-

gregate and a minor amount of a salt of a long chain aliphatic hydrocarbon amine and an alkali metal amine and water-soluble inorganic acid phosphate, said salt being substantially insoluble in asphalt and in water and being present at least in an amount sufficient to improve the adhesion of the asphalt to said wet aggregate.

2. An asphalt composition comprising an asphalt, a wet aggregate and a salt of a long chain aliphatic hydrocarbon amine and chromic acid, said salt being substantially insoluble in asphalt and in water, and being present at least in an amount sufficient to improve the adhesion of the asphalt to said wet aggregate.

3. An asphalt composition comprising an asphalt, a wet aggregate and an acid phosphate salt of the hydrogenated polyamine condensation product of ammonia and acrolein, said condensation product being in the form of a partial amide with oleic acid, said acid phosphate salt thereof being substantially insoluble both in asphalt and in water, and being present at least in an amount sufficient to improve the adhesion of the asphalt to said wet aggregate.

4. An asphalt composition comprising an asphaltic material, a solid and, at the interface therebetween, a salt selected from the group consisting of phosphates and chromates of a long chain aliphatic hydrocarbon amine being substantially insoluble both in water and in asphalt, and being present at least in an amount sufficient to improve the adhesion of asphaltic material to the solid.

5. An asphalt composition comprising an asphaltic material, a wet solid and small amount of a reaction product of a long chain aliphatic hydrocarbon amine with a water-soluble acid-acting agent having a polyvalent anion and having only a monovalent cation, said amount being sufficient to improve the bonding power of the asphalt said reaction product being insoluble in asphalt and water and forming a rigid interfacial film between the solid and the asphalt.

6. An asphalt composition consisting essentially of an asphaltic material, a solid and, at the interface therebetween, the reaction product of octadecylamine and potassium dihydrogen phosphate, said reaction product being substantially insoluble both in water and in asphalt and being present at least in an amount sufficient to improve the adhesion of asphaltic material to the solid.

7. An asphalt composition consisting essentially of an asphaltic material, a solid and, at the interface therebetween, a salt reaction product of a long chain aliphatic hydrocarbon amine and potassium dihydrogen phosphate, said reaction product being substantially insoluble both in water and in asphalt and being present at least in an amount sufficient to improve the adhesion of asphaltic material to the solid.

8. An asphalt composition comprising an asphaltic material, a solid and, at the interface therebetween, a salt reaction product of octadecylamine and chromic acid, said reaction product being substantially insoluble both in water and in asphalt and being present at least in an amount sufficient to improve the adhesion of asphaltic material to the solid.

9. An asphalt composition comprising an asphaltic material, a solid and, at the interface therebetween, the salt reaction product of an oleic acid partial amide of a hydrogenated polyamine condensation product of acrolein and ammonia with potassium dihydrogen phosphate,

said reaction product being substantially insoluble both in water and in asphalt and being present at least in an amount sufficient to improve the adhesion of asphaltic material to the solid.

10. An asphalt composition comprising an asphaltic material, a solid and at the interface therebetween an amine salt of a water-soluble acid-acting agent, wherein the amine is selected from the group consisting of (1) a long chain aliphatic hydrocarbon amine and (2) an oleic acid partial amide of a hydrogenated polyamine condensation product of acrolein and ammonia and the acid-acting agent is composed of a polyvalent anion and only monovalent cations, said amine salt being substantially insoluble both in water and in asphalt and being present at least in an amount sufficient to improve the adhesion of the asphalt to the solid.

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