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ASPHALT COMPOSITIONS

Mathew L. Kalinowski, Chicago, and Lowell T. Crews, Homewood, Ill., and Frederick H. MacLaren, Munster, Ind., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

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The present invention is directed to improvements in bitumen compositions and particularly to improvements in mineral aggregate coating compositions, and more particularly relates to bitumen compositions having improved adherence to damp or wet mineral aggregates.

Residual oils and/or bituminous materials used in the preparation of pavements and roads do not coat and adhere well to mineral aggregates unless the aggregate is substantially dry, and for this reason, in conventional pavements or road construction practice, it is customary to dry the mineral aggregate by suitable well known methods. Furthermore, water entering the road or pavement during service may have a detrimental effect in that it may displace the oil or bitumen from the surface of the aggregate and thus diminish the bonding effect of the oil and/or bitumen. This materially shortens the life of the road or pavement requiring frequent repairs and is, therefore, uneconomical.

Mineral aggregates employed in road or pavement construction, range in character from hydrophilic to hydrophobic. In general, siliceous and acidic minerals, such as sands and gravels, tend to be hydrophobic, while calcareous alkaline minerals, such as limestone, tend to be hydrophilic. It has been observed that the mineral aggregates appear to have a greater attraction for water than for oil or bitumens and that it is difficult to obtain, by conventional methods, complete or satisfactory coating of aggregates by oil or bitumen when water is present. Furthermore, even though satisfactory coating is obtained by using dry aggregate, the oil or bitumen tends to be displaced if water enters the pavement or road.

It is known that the coating of damp or wet mineral aggregates by oil or bitumen may be effected and the resistance of the coating to displacement or stripping by water may be improved by treating the aggregate with small amounts of a water-soluble soap of a fatty acid in conjunction with water-soluble salt of a polyvalent heavy metal or "activator." For optimum results with these reagents the relative amounts of the two reagents must be carefully adjusted. Thus, when a divalent heavy metal is used as activator, the amount of soap used should be substantially one mole per mole of activator; with a trivalent metal, between one and two moles of soap per mole of activator. Use of larger amounts of soap than this diminishes the effect obtained and this diminution of effect increases with excess of soap over the proportions given until, when the amount of soap becomes equivalent to the activator, i. e., two moles of soap per mole of divalent metal or three per mole of trivalent metal the beneficial effect of the reagent substantially disappears.

The above method has the disadvantage that the relative amounts of soap and polyvalent heavy metal activator are critical and must be carefully adjusted for optimum results. Use of an excess of soap over the optimum amount diminishes rather than enhances the effect obtained; the use of excess heavy metal to avoid the danger of excess soap is not harmful but increases the cost. Furthermore, the two reagents must be weighed

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or measured out and added to each batch, as neither is soluble in the oil or bitumen; while this disadvantage may be partially overcome under favorable conditions by using in place of the soap a fatty acid dissolved in the oil or bitumen, this expedient is effective only under favorable conditions of low moisture content of the aggregate, adequate and efficient mixing, etc. Under the conditions which are not at all severe, such as appreciable amounts of water and/or facilities for only moderately efficient mixing, fatty acids appear not to be sufficiently soluble in water to reach and react with the heavy metal ion to the required extent, and if added directly to the mixture or dissolved in the oil or bitumen, are practically without effect.

Another important disadvantage of the above method is that a heavy polyvalent metal salt must be used with the soap. Furthermore, it has been found that while some limestones appear capable of adsorbing or reacting with polyvalent metal ions and accordingly respond to some degree to the above method, a great many others do not, and with these it is difficult or impossible to obtain a good coating by the above method. Also, since the foregoing method is not in general satisfactory with limestone, a great many natural mixed aggregates, such as gravels containing both siliceous and calcareous particles will have only a portion of the particles coated.

In addition to the use of polyvalent fatty acid soaps in bitumens as mineral aggregate coating agents, certain organic nitrogen compounds, such as those obtained by reacting a polyamine with a fatty acid under conditions to form essentially amides, have been used for this purpose. However, although the amide-type asphalt additives are effective coating agents for acidic mineral aggregates, such as sands and gravels they are ineffective on alkaline mineral aggregates, such as limestone.

It is an object of the present invention to provide a bituminous material having improved coating properties. It is also an object of the present invention to provide an oil or bitumen composition which will adhere to wetted acidic and alkaline mineral aggregates. Another object of the invention is to provide a coating composition for acidic and alkaline mineral aggregates which will not be stripped therefrom by aqueous liquids. Still another object of the invention is to provide a coating composition for acidic and alkaline mineral aggregates which can be applied without the necessity of drying the mineral aggregate and which will adhere thereto even in a wet condition. Another object of the invention is to provide a method of preventing stripping of the coating composition from acidic and alkaline mineral aggregates by water after the road and/or pavement is constructed. A further object of the invention is to provide a method of promoting the adherence of oil bituminous materials to siliceous and limestone aggregates without the necessity of drying the same. Other objects and advantages of the invention will become apparent from the following description thereof.

In accordance with the present invention, bitumens such as for example, road oils and asphalts having improved mineral aggregate coating properties, especially with respect to wet acidic and alkaline mineral aggregates, are obtained by incorporating in such bitumens from about 0.25% to about 5%, and preferably from about 0.5% to about 3%, by volume, of the oil-soluble product obtained by reacting an aliphatic polyamine with a carboxylic acid pitch selected from the group consisting of tall oil pitch and hydrogenated fish oil fatty acid pitch, under conditions which avoid the formation of amides so that a product essentially free of the latter is obtained. Since amidation of amine soaps is brought about by the loss of water at high temperatures the reaction of the alkylene polyamine with the aforementioned pitches is

carried out at temperatures below about 265° F., preferably below about 240° F., and more preferably at temperatures of from about 180° F. to about 225° F.

The tall oil pitch is a residue or bottoms fraction produced in the vacuum distillation of whole tall oil and comprises essentially fatty acids, rosin acids and unsaponifiables, such as sterols, higher alcohols and other unsaponifiable matter. The fatty acid fraction contains oleic acid, linoleic acid, palmitic acid, and other higher fatty acids. The rosin acid fraction comprises a mixture of a number of different structural forms of rosin acids including a large proportion of abietic acid and neoabietic acid. A typical tall oil pitch will have the following specifications:

Acid No.	60-75
Saponification No.	90-100
Rosin acids No.	45-60
Iodine No.	115-135
Fatty acids	35-50%
Rosin acids	15-32%
Unsaponifiables ¹	22-40%

¹ Sterols, higher alcohols, esters, etc.

The hydrogenated fish oil fatty acid pitch referred to as marine pitch, is obtained as a residue fraction in the distillation of hydrogenated fish oils. In one method of preparing the marine pitch the fish oil, which may be for example, sardine oil, herring oil, cod oil, menhaden oil, etc., is first split by any of the well known methods to produce glycerine and fatty acids. After separation of the glycerine, the fatty acids are hydrogenated, subsequently distilled to produce an overhead distillate of hydrogenated fish oil fatty acids and a residue or pitch. This pitch or residue in which are concentrated fatty materials may be employed as such for the herein described purpose; or it may be subjected to a splitting operation to produce more glycerine and hydrogenated fatty acids. After separation of the glycerine the hydrogenated fatty acids are distilled to produce an overhead product of hydrogenated fish oil fatty acids and a residue or bottoms fraction which is referred to as marine pitch. The marine pitches are rich in saturated fatty acids of about 12 to 24 or more carbon atoms.

The tall oil pitch and the hydrogenated fish oil fatty acid pitch or marine pitch are referred to hereinafter generically as "pitch."

The amine reactant employed in preparing the additive of the present invention is an aliphatic polyamine, particularly an alkylene polyamine containing at least two primary amino nitrogen atoms. Examples of alkylene polyamines suitable for the herein-described purpose are ethylene diamine, propylene diamine, diethylene triamine, diamylene triamine, triethylene tetramine, tripropylene tetramine, diethylenepropylene tetramine, tetraethylene pentamine, tetrabutylene pentamine, diethylenedipropylene pentamine, butylene diamine, dihexylene triamine, and the like or mixtures thereof. For example, a suitable polyamine product is a crude diethylene triamine containing minor amounts of ethylene diamine and triethylene tetramine. Other suitable polyamines include those having the general formula $RNH(CH_2)_nNH_2$, in which R is preferably a C_{10} to C_{18} aliphatic chain and which are obtained by condensing the suitable amine with acrylonitrile and hydrogenating to the corresponding diamine. Commercially available polyamines of this type are those marketed by Armour and Company as "Duomeens," which are prepared by the condensation of a dodecyl (Coco) amine or an octadecyl (tallow) amine with acrylonitrile followed by hydrogenation to the corresponding diamine product; these products are marketed as "Duomeen C" and "Duomeen T," respectively.

In the preparation of the pitch and polyamine reaction product, it is preferable, although not essential, that the pitch be first dehydrated to obtain an essentially water-free product, or a product having not more than about

0.5% water. This can be readily accomplished by diluting the pitch with from about 10% to about 50% of a suitable hydrocarbon solvent, preferably a solvent rich in aromatic hydrocarbons and by heating the diluted mixture at a temperature of about 210° F. to 290° F. while stirring and/or blowing with air or other suitable gaseous medium until the water content has been reduced to the desired value. If the pitch contains an undesirable amount of contaminants they can be removed by permitting the hot solution to settle and decanting the diluted solution of purified pitch. If desired, the diluent may be removed from the dehydrated pitch by suitable means such as by distillation under vacuum; however, we prefer to react the diluted pitch with the polyamine.

Aromatic-rich hydrocarbon solvents suitable for this purpose are preferably those having boiling points above about 220° F. at atmospheric pressure and includes mono-nuclear aromatic hydrocarbons or condensed ring aromatics, such as naphthalenes and mixtures of the higher boiling mono-nuclear aromatic hydrocarbons and polynuclear aromatic hydrocarbons.

A preferred source of mixed aromatic hydrocarbons suitable for this purpose is a light catalytic cycle stock obtained from a powdered or a fluid-type catalytic-type hydrocarbon cracking operation in which gas oil or heavier hydrocarbons are cracked at a temperature of 800° F. to 1050° F. under a pressure of about atmosphere to 50 pounds per square inch and in the presence of suitable fluid or powdered catalyst, such as for example, silica-alumina, silica-magnesia and other well known cracking catalysts. A method of conducting a fluidized cracking operation is described in U. S. 2,341,193 issued to Fred W. Scheineman February 8, 1944. Fractions from the process heavier than gasoline, depending upon their boiling range, are commonly referred to as light catalytic cycle stock, heavy catalytic cycle stock and catalytic recycle resid, which usually are cycled to cracking. A light catalytic cycle stock particularly well suited as a diluent for the dehydration of the pitch is a fraction having an aromatic content of at least about 40% and a distillation range between about 425° F. and about 560° F. A typical analysis of a suitable light catalytic cycle stock shows the material to be composed substantially of about 10% normal C_{12} to C_{20} paraffins, about 45% of other paraffins and naphthenes, about 5% mono-nuclear aromatics which are mainly mono- to hexa-alkylated benzenes, and about 40% polynuclear aromatics which are mainly alkyl naphthalenes, largely methylated naphthalenes. While we prefer to use a light catalytic cycle stock of the type described, hydrocarbon fractions from other catalytic conversion processes or thermal hydrocarbon conversion processes are suitable, provided they have an aromatic content of at least 20% and a distillation range above about 220° F.

The dehydrated pitch preferably but not necessarily in solution in the light catalytic cycle stock or other suitable diluent is reacted with the polyamine in the ratio of from about 25:1 to about 5:1, and preferably in a ratio of from about 12:1 pitch to the polyamine at a temperature below about 265° F., and preferably of from about 180° F. to about 225° F. for not more than about one hour, preferably one-half hour, and the temperature then reduced as rapidly as possible to about 170° F., or lower. By conducting the reaction in the manner herein-described and maintaining the finished product until ready for use at a temperature below about 150° F., and preferably below about 140° F., an efficient, stable coating agent essentially free of amido groups is obtained.

Under some conditions the polyamine-pitch reaction product even in solution in the diluent, such as the light catalytic cycle stock, may cause some difficulty in the pumping and transfer thereof from containers and through pipelines, especially when the temperature falls below about 70° F.-80° F. This condition can be corrected by adding from about 5 parts to about 15 parts of an ali-

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phatic alcohol of less than about five carbon atoms, preferably isopropyl alcohol, to the mixture of pitch-polyamine reaction product and hydrocarbon diluent. A suitable mixture comprises from about 40 parts to about 60 parts of the pitch-polyamine reaction product, from about 55 parts to about 25 parts of the light catalytic cycle stock, and from about 5 parts to about 15 parts isopropyl alcohol.

The preparation of polyamine-pitch reaction products is illustrated by the following examples:

EXAMPLE I

One hundred parts of tall oil pitch was dissolved in 50 parts of light catalytic cycle stock and the mixture heated to a temperature of 210° F.-240° F. Four parts of ethylenediamine were added to the heated mixture of tall oil pitch and cycle stock and the reaction mass maintained at a temperature of 210° F.-240° F. for one hour, and then rapidly cooled.

EXAMPLE II

152 parts of tall oil pitch, equivalent weight 775, was dissolved in 108 parts of light catalytic cycle stock and the mixture was heated to 210° F. Nine and three-fourths parts of 75% ethylenediamine were added to the heated mixture of tall oil pitch and cycle stock and the reaction mass maintained at a temperature of 190° F.-210° F. for fifty minutes, and then rapidly cooled.

EXAMPLE III

149 parts of tall oil pitch, equivalent weight 775, was dissolved in 106 parts of light catalytic cycle stock and the mixture was heated to 206° F. Thirteen and one-fourth parts of 85% crude diethylenetriamine were added to the heated mixture of tall oil pitch and cycle stock and the reaction mass maintained at a temperature of 210° F. for one hour, and then rapidly cooled.

EXAMPLE IV

308 parts of marine pitch, equivalent weight 616, was stirred, heated and blown with 154 parts of light catalytic cycle stock at a temperature of 220° F.-240° F. for about 30 minutes. Blowing of the mixture was stopped and 23 parts of 75% ethylenediamine (115% of the amount needed to neutralize the free acid in the pitch) was added and the mixture stirred at 220° F.-240° F. for one hour, and then cooled.

EXAMPLE V

Same as Example IV, except 130% of the calculated ethylene diamine was added.

EXAMPLE VI

Same as Example IV except triethylene tetramine was substituted for the ethylenediamine.

The asphalt component of the herein-described composition may be of any bitumen which is useful for the coating of mineral aggregates used in the making of roads, highways, etc., or for the coating of other materials or surfaces where a water-resistant bond between the surface and the asphalt is advantageous, or necessary. The term "asphalt" as employed herein is intended to be synonymous with bitumen and to cover a liquid, semi-solid, or solid plastic bituminous material of the type employed in making or surfacing of highways and/or pavements, caulking agents, sealing compounds, water impervious paints, roofing materials, etc. Such asphalts or bituminous materials are mixtures of hydrocarbons of natural or pyrogenous origin, and are usually derived from petroleum or coal but may occur as such in nature. Asphalts may be derived as distillation resids or cracking resids with or without oxidation by air-blowing or by catalytic oxidation. The specific example of an asphalt of the type usually employed in the preparation of highways, etc. is a petroleum residuum cutback, fluxed with a light aromatic dilu-

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uent boiling in the range of 400° F. to 700° F. to give a cutback product of the following specifications:

	Cutback asphalt
Flash, ° F. (C. O. C.)	NLT* 150.
Viscosity, furol at 140° F.	100-200.
A. S. T. M. distillation:	
Percent off at 437° F.	NMT** 10.0.
Percent off at 500° F.	15-55.
Percent off at 600° F.	60-87.
Residue at 680° F.	NLT 67.0.
Tests on distillation—	
Residue:	
A. S. T. M. penetration at 77° F.	120-300.
A. S. T. M. ductility at 77° F.	NLT 100.
Sol. in CCl ₄ , percent.	NLT 99.5.
Oliensis spot test.	Negative.

* "Not less than."

** "Not more than."

Normally solid paving asphalts of the 40-200 penetration grades commonly used in road building fall within the following specifications:

Penetration at 77° F.	40-200.
A. S. T. M. ductility at 77° F.	Not less than 100.
Oliensis spot test.	Negative.
Solubility in CCl ₄ , percent.	Not less than 99.5.
Specific gravity at 60° F.	Not less than 0.990-1.000.
Flash, ° F. (C. O. C.)	Not less than 475.
Loss on heating 50 grams for 5 hours at 325° F., percent.	Not more than 0.5.
Penetration of residue at 77° F., percent of original penetration.	Not less than 70-75.

The effectiveness of the herein-described pitch-polyamine reaction products in enhancing the adhesion of asphalts to wet mineral aggregates is determined by subjecting blends of asphalts and the described reaction products to one or more of the following tests:

A. Modified Colorado coating tests

20 grams of Ottawa sand or 20 grams of a 20 to 35 mesh limestone are weighed into a 2 oz. container and covered with one-half inch of distilled water. One gram of the additive-containing asphalt is floated on the water, the mixture then shaken for thirty seconds, and the extent of coating is determined by visual inspection; the results are expressed as "percent coated."

B. Wyoming stripping test

Approximately 25 g. of Lander chips, all passing the 3/8 inch sieve and retained on the No. 4 sieve, is mixed by hand with 1.0 g. of fortified asphalt until the best possible coating is obtained. The mix is placed in an oven at 140° F. for eighteen to twenty-four hours, after which it is thoroughly remixed and is allowed to cool to room temperature. The sample is then immersed in distilled water at a temperature of 120° F., and is maintained at this temperature for a period of twenty-four hours. At the end of this period the area of the aggregate remaining coated is determined visually while the sample is still under water. Any thin or translucent areas are considered to be coated. The Wyoming Highway Department requires that 80% or greater coating be retained in this test.

C. Hot settling test

300 grams of asphalt containing 2% of the additive are stored in a closed one pound tin container at 170° F. for twenty-four hours. At the end of this period the percent of sediment is determined gravimetrically. A value less than 2% is considered desirable. The asphalt-additive mixture, after being stored at 170° F. for the twenty-four

hour period, is retested by the Colorado Coating Test (supra) for its ability to coat wet aggregates.

The data obtained by subjecting blends of asphalt and reaction products of polyamines and tall oil pitches or marine pitch, prepared in the manner herein-described, to one or more of the above-described tests, are given in Table I.

TABLE I

Additive	Colorado Coating Test		Wyoming Stripping Test, percent	Sediment, percent	Hot Settling Test Colorado Coating	
	Sand, percent	Limestone, percent			Sand, percent	Limestone, percent
Control (none)-----	0	0	10	0	0	0
Control +2% "A"-----	100	90	85	0.1	100	90
Control +1% "B"-----	100	80	85	0	95	80
Control +2% "B"-----	100	80	90	0.1	100	80
Control +2% "C"-----	100	100	100	0.0	100	100
Control +2% "D"-----	100	90	100	0.0	100	90
Control +2% "E"-----	100	95	100	0	100	95
Control +2% "F"-----	100	100	95	0	0	10
Control +2% "G"-----	100	100	100	0.1	10	15

In Table I the various additives are identified as follows:

In Table I the various additives are identified as follows:

"A"—Tall oil pitch reacted with 2 equivalents ethylenediamine in the manner above-described.

"B"—Tall oil pitch reacted with 3 equivalents ethylenediamine in the manner above-described.

"C"—Marine pitch reacted with 1.15 equivalents ethylenediamine prepared as in Example IV.

"D"—Marine pitch reacted with 1.3 equivalents ethylenediamine prepared as in Example V.

"E"—Marine pitch reacted with 1.15 equivalents triethylenetetramine prepared as in Example VI.

"F" and "G"—Commercial asphalt coating agents comprising essentially fatty acid-polyamine amides.

The data in Table I demonstrate the stability and the effectiveness of the reaction products of a polyamine and tall oil pitch or marine pitch, prepared in the manner herein-described for maintaining asphalt coatings on both wet acidic and alkaline mineral aggregates. The hot settling data with respect to additives "F" and "G," commercial asphalt additives comprising essentially fatty acid-polyamine amides, demonstrate the instability of such products.

Although the pitch-polyamine reaction products are heat stable at temperatures as high as 230° F. and exhibits essentially no degradation with respect to coating and stripping efficiency, it is advisable to limit the blending and/or storage temperature for the fortified asphalts to temperatures not in excess of about 150° F., and preferably at temperatures not in excess of 140° F. Likewise, asphalts containing the herein-described asphalt additives should preferably be applied at temperatures not to exceed about 230° F.

Concentration percentages expressed herein are volume percentages unless otherwise specified.

While the present invention has been described by reference to specific embodiments thereof, these are given by way of illustration only and the invention is not to be limited thereto but includes within its scope such modifications and variations as come within the spirit of the appended claims.

We claim:

1. A bitumen composition consisting essentially of a major proportion of a bitumen and from about 0.25% to about 5% of the oil-soluble reaction product essentially free of amido groups obtained by reacting an aliphatic polyamine and a carboxylic acid pitch selected from the group consisting of tall oil pitch and hydrogenated fish oil fatty acid pitch at a temperature of from about 180° F. to about 265° F. for not more than about one and one-half

hours, and then rapidly reducing the temperature to below about 170° F.

2. A bitumen composition described in claim 1 in which the aliphatic polyamine is an alkylene polyamine containing at least two primary amino nitrogen atoms.

3. A bitumen composition described in claim 1 in which the aliphatic polyamine is an alkylene diamine.

4. A bitumen composition described in claim 1 in which the aliphatic polyamine is ethylene diamine.

5. A bitumen composition described in claim 1 in which the aliphatic polyamine is propylene diamine.

6. A bitumen composition described in claim 1 in which the aliphatic polyamine is diethylene triamine.

7. A bitumen composition described in claim 1 in which the aliphatic polyamine is a polyamine mixture comprising essentially diethylene triamine and minor amounts of ethylene diamine and triethylene tetramine.

8. A bitumen composition described in claim 1 in which the aliphatic polyamine is trialkylene tetramine.

9. A bitumen composition described in claim 1 in which the aliphatic polyamine is triethylene tetramine.

10. A bitumen composition described in claim 1 in which the aliphatic polyamine has the general formula $RNH(CH_2)_3NH_2$, in which R is an hydrocarbon group containing from about 10 to about 18 carbon atoms, said polyamine being obtained by condensing a C_{12} to C_{18} aliphatic amine with acrylonitrile and hydrogenating the condensation product to the corresponding diamine.

11. A bitumen composition described in claim 1 in which the bitumen is normally liquid bitumen.

12. A bitumen composition as described in claim 1 in which said reaction product is diluted with from about 10% to about 50% of an aromatic-rich hydrocarbon diluent having a boiling point above about 220° F.

13. A bitumen composition as described in claim 1 in which the bitumen is a normally solid paving asphalt.

14. A bitumen composition consisting essentially of a major proportion of a bitumen and from about 0.25% to about 5% of the oil-soluble reaction product essentially free of amido groups obtained by reacting an alkylene polyamine and tall oil pitch at a temperature of from about 180° F. to about 265° F. for not more than about one and one-half hours, and then rapidly reducing the temperature to below about 170° F.

15. A bitumen composition consisting essentially of a major proportion of a bitumen and from about 0.25% to about 5% of the oil-soluble reaction product essentially free of amido groups obtained by reacting an alkylene polyamine and a hydrogenated fish oil fatty acid pitch at a temperature of from about 180° F. to about 265° F. for not more than about one and one-half hours, and then rapidly reducing the temperature to below about 170° F.

16. A coating composition comprising from about 40 parts to about 60 parts of the oil-soluble reaction product of an alkylene polyamine and a carboxylic acid pitch selected from the group consisting of tall oil pitch and hydrogenated fish oil fatty acid pitch, said reaction product being essentially free of amido groups, from about 25 parts to about 55 parts of an aromatic-rich

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hydrocarbon diluent having a boiling point above about 220° F., and from about 5 parts to about 15 parts of an aliphatic alcohol having less than about 5 carbon atoms, said oil-soluble reaction product being obtained by reacting said alkylene polyamine and said carboxylic acid pitch at a temperature of from about 180° F. to about 265° F. for not more than about one and one-half hours, and then rapidly reducing the temperature to below about 170° F.

17. A roadway construction material resistant to water stripping comprising mineral aggregates admixed with a coating composition consisting essentially of a major proportion of a normally liquid bitumen and from about 0.25% to about 5% of the oil-soluble reaction product of an alkylene polyamine and a carboxylic acid pitch selected from the group consisting of tall oil pitch and a hydrogenated fish oil fatty acid pitch, said reaction product being essentially free of amido groups and obtained by reacting said alkylene polyamine and said carboxylic acid pitch at a temperature of from about 180° F. to about 265° F. for not more than about one and one-half hours, and then rapidly reducing the temperature to below about 170° F.

18. The method of forming a water-resistant bond

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between mineral aggregates and a bitumen comprising incorporating in said bitumen from about 0.25% to about 5% of an amido-free oil-soluble reaction product of an aliphatic polyamine and a carboxylic acid pitch selected from the group consisting of tall oil pitch and hydrogenated fish oil fatty acid, and applying said mixture to said mineral aggregates, said oil-soluble reaction product being obtained by reacting said polyamine and said carboxylic acid pitch at a temperature of from about 180° F. to about 265° F. for not more than about one and one-half hours, and then rapidly reducing the temperature to below about 170° F.

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