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(54) Title: CATIONIC ACRYLAMIDE AND RUBBER MODIFIED ASPHALTS

(57) Abstract

Cationic chemically modified asphalts having utility for road constuction, repair and maintenance as well as coating for various substrates, including cementitious substrates, glass and metal. These asphalts are the product produced by reacting an acrylamide, asphalt, a vinyl aromatic monomer and a rubbery polymer.

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D E S C R I P T I O N

CATIONIC ACRYLAMIDE AND RUBBER MODIFIED ASPHALTS

TECHNICAL FIELD

The present invention relates to asphalt compositions, and more particularly it relates to chemically modified asphalt compositions. Even yet more particularly, the present invention relates to acrylamide modified asphalts.

BACKGROUND ART

Asphalt has been employed for numerous and wide variety of applications for many years. One of the problems encountered with asphalt is that its adhesion to various substrates and especially to aggregate needs to be improved. Such aggregate is represented, for example, by gravel, crushed rock, slag, sand and crushed limestone. Additionally, the adhesion of asphalt needs to be improved with respect to other material such as, for example, cementitious materials, metals, glass and the like.

DISCLOSURE OF THE INVENTION

An improved chemical composition is provided in accordance with this invention, which composition is the product produced by reacting an acrylamide with asphalt, and a vinyl aromatic monomer and a rubbery polymer.

Some of the desirable properties of the present compositions include improved coatability of negatively charged surfaces, improved adhesion, less stripping, improved emulsifiability, improved flexibility, particularly at low temperatures, improved strength,

reduced high temperature flow, increased durability, better compatibility with polymers.

The compositions of the present invention are obtained by heating at an elevated temperature for several hours. Preferably, the reacting is done by heating at a temperature of at least about 120°C for about 10 hours, and most desirably, at a temperature of about 160°C to about 180°C for about 20 hours.

The acrylamides employed in the present invention may desirably be secondary amides or tertiary amides. Preferably, the acrylamide will be a compound of the formula

$$(R_1)(R_2)C = C(R_3) - C(O)N(R_4)(R_5)$$

wherein R_1, R_2 and R_3 are independently selected from hydrogen or an alkyl containing 1 to 3 carbon atoms; R_4 and R5 are independently selected from hydrogen, an alkyl containing 1 to 3 carbon atoms, or preferably a radical of the formula

$$-R_6 - N(R_7)(R_8)$$

wherein R_7 and R_8 are independently selected from hydrogen or an alkyl having 1 to 3 carbon atoms, and R_6 is an alkylene group containing 1 to 5 carbon atoms. The preferred acrylamide is dimethylaminopropylmethacrylamide, that is a compound of the formula

$$CH_2 = C(CH_3)C(O)N(H)(CH_2)_3N(CH_3)_2$$

The above-type acrylamides, as will be apparent, contain a double bond. It will be found that the presence of this double bond provides for the ability to chemically incorporate the acrylamide into the composition. Additionally, the amino groups present in the acrylamides provide for highly desirable polarity which serves to greatly enhance the adhesive bonding of the present compositions to various substrates, including, for example, aggregates commonly employed in road repair and maintenance, as well as cementitious and other substrates. Representative acrylamides include N,N-dimethylaminopropylmethacrylamide,

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Asphalt materials which are suitable for these purposes preferably include those which are typically used for road paving, repair and maintenance purposes. Thus, asphalt includes natural asphalt, petroleum asphalt and petroleum tar. The natural asphalts include, for example,

asphaltite, such as Gilsonite, grahamite and glancepitch, lake asphalt, such as Trinidad asphalt, and rock asphalt. The petroleum asphalt that may be used includes straight asphalt obtained by distillation of a crude oil, blown asphalt, produced by blowing an oxygen-containing gas into straight asphalt, and solvent extracted asphalt. The petroleum tar that may be used includes coal tar and oil gas tar. Tar pitch is equally suitable. Additionally, the asphalts can be those that have been blown with steam, ammonia, or amines. Preferably, the asphalt which will be employed is an asphalt cement of the type typically used for road paving, repair and maintenance purposes, such as for example, the AC-5, AC-10, AC-20 grades. Such asphalts typically have penetrations ranging between about 20 to about 200.

As the polymerizable vinyl monomer, use is preferably made of a monofunctional vinyl aromatic monomer having a general formula:

$$R_1 - C = C - R_3$$
$$\quad\quad R_2 \quad R_2$$

wherein R_1 is an aromatic group containing 6 to 12 carbon atoms, including a phenyl group, a substituted phenyl group wherein the substituent is any one of an amino group, a cyano group, a halogen group, a C_1 to C_3 alkoxy group, a C_1 to C_3 alkyl group, a hydroxy group, a nitro group, etc. R_2 is preferably hydrogen or lower alkyl e.g., a C_1 to C_5 alkyl and R_3 is hydrogen, lower alkyl or one of the following groups:

$$-CH_2OH, \; -CHO, \; -\overset{O}{\overset{\|}{C}}-X, \; -\overset{O}{\overset{\|}{C}}-OH, \text{ or } -CH_2-CN$$

wherein X is halogen, and preferably chlorine or bromine. Styrene is preferred. In conjunction with the vinyl aromatic monomer as described above, a polyfunctional vinyl aromatic monomer containing 6 to 12 carbon atoms in the aromatic ring and two or more polymerizable vinyl groups

chemically bonded to the aromatic ring can optionally be employed. Preferred polyfunctional monomers are those having the general formula:

$$CH_2 = CH - R_4 - \underset{R_5}{C} = CH - R_6$$

wherein R_4 is a divalent aromatic group containing 6 to 12 carbon atoms, and preferably a phenylene group; and, R_5 and R_6 have the same meaning as is described above with respect to R_2 and R_3, respectively for the monofunctional vinyl aromatic monomer. Illustrative of a suitable polyfunctional vinyl aromatic monomer is divinyl benzene. When use is made of a polyfunctional vinyl aromatic monomer in combination with a monofunctional vinyl aromatic monomer such as styrene, generally the monofunctional vinyl aromatic is present in a weight ratio of about 1:1 to 40:1 based on the weight of the polyfunctional vinyl aromatic monomer.

As the rubbery polymer, use can be made of a number of vulcanizable elastomeric materials well known to those skilled in the art. Included are natural rubbers as well as synthetic rubbers. Suitable are synthetic rubbers which are homopolymers of a conjugated diene (e.g., butadiene, isoprene, chloroprene, etc.) as well as various polymers which are substituted with a functional group containing a labile hydrogen atom. For example, various hydroxy, amino and like substituted homopolymers of conjugated dienes may likewise be used in the practice of this invention. Substituted butadienes are commercially available from, for example, Atlantic-Richfield under the trademark "Poly B-D", a series of hydroxy-terminated butadiene polymers; for example, use can be made of hydroxy-terminated butadiene homopolymers like Poly B-D R-15M which has a hydroxy number of 42 or Poly B-D R-45M.

Preferably, the rubber polymer is an elastomeric material formed by copolymerization of one or more of the conjugated dienes described above with one or more

ethylenic monomers such as styrene as well as hydroxy, amino and mercapto-substituted derivatives thereof, acrylonitrile, methacrylonitrile, acrylic acid, methacrylic acid, etc. Included are butadiene-styrene rubbers, butadiene-acrylonitrile rubbers, etc. Hydroxy-terminated copolymers are likewise useful in the practice of this invention, including the hydroxy-terminated butadiene-styrene copolymer designated "Poly B-D CS-15" and hydroxy-terminated butadiene-acrylonitrile copolymers like Poly B-D CN-15 having a hydroxyl number of 39. Preferred are butadiene-styrene rubbers like SOLPRENE 1205C available from Phillips Petroleum.

The amount of the various ingredients may vary over a wide range. Preferably, however, the acrylamide will be employed in an amount of about 0.5 to about 15% based on the weight of asphalt, the vinyl aromatic will be used in an amount of about 0.5 to about 35% based on the weight of the asphalt, and the rubbery polymer will be employed in an amount of about 0.5 to about 30% based on the amount by weight of asphalt.

While the above describes the invention with sufficient particularlity to enable those skilled in the art to make and use same, nonetheless further examplification follows.

BEST MODE OF CARRYING OUT INVENTION

Example

Using a charge of about 67.5% of AC-20 asphalt, 5% by weight of dimethylaminopropylmethacrylamide, about 15% by weight of styrene, and about 12.5% by weight of Solprene 1205C rubber, a composition is produced as follows. Into a reactor equipped with an agitator and a reflux condenser, the asphalt is charged and heated to approximately 110°C at which time styrene is charged into the reactor. The reactor is then heated to a temperature of about 150°C during which time the acrylamide and the rubber is charged into the reactor. The ingredients are then heated at a temperature of about 150°C with agitation

and under reflux for about 24 hours. This product when cooled is suitable for any of the varied utilities previously set forth.

INDUSTRIAL APPLICABILITY

These compositions will find utility for a wide variety of purposes. They, for example, will find application in the highway and bridge construction, repair and maintenance areas as, for example, crack and pothole fillers, joint sealers, and water resistant membranes, as well as cut-backs with the compositions being used alone or as blends with conventional asphalts. These compositions can be formed into emulsions with conventional asphalt emulsifiers to form a slow set emulsion, having utility for slurry seal applications, or as a cold overlay. Preferably non-ionic surfactants are used as emulsifiers. The compositions may also be employed as corrosion resistant and/or water resistant coatings for metals and as coatings and/or impregnants for glass, especially glass fibers. Such coated or impregnated glass fibers will show outstanding compatibility with conventional asphalt and consequently will serve as outstanding reinforcements for such asphalts.

C L A I M S

1. As a composition of matter, the product produced by reacting an acrylamide, asphalt, a vinyl aromatic monomer and a rubbery polymer.

2. The composition of claim 1 wherein said acrylamide is a compound of the formula

$$(R_1)(R_2)C = C(R_3) - C(O)N(R_4)(R_5)$$

wherein R_1, R_2 and R_3 are independently selected from hydrogen and a C_1-C_3 alkyl; R_4 and R_5 are independently selected from hydrogen, a C_1-C_3 alkyl and a radical of the formula

$$-R_6-N(R_7)(R_8)$$

wherein R_6 is an alkylene group of 1 to 5 carbon atoms and R_7 and R_8 are independently selected from hydrogen or a C_1-C_3 alkyl.

3. The composition of claim 2 wherein R_5 is said radical of the formula $-R_6-N(R_7)(R_8)$.

4. The composition of claim 3 wherein R_1 and R_2 are hydrogen.

5. The composition of claim 3 wherein R_6 is ethylene or propylene.

6. The composition of claim 3 wherein R_3, R_7 and R_8 are hydrogen or methyl.

7. The composition of claim 2 wherein said acrylamide is dimethylaminopropylmethacrylamide.

8. The composition of claim 2 wherein said rubbery polymer is a homopolymer of a diene or a copolymer of a diene and an olefinically unsaturated monomer.

9. The composition of claim 8 wherein said reacting is done by heating at a temperature of at least about 120°C for at least about 10 hours.

10. The composition of claim 8 wherein said vinyl aromatic is styrene.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US82/01625

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC 3

C08F 289/00; C08G 83/00; C08H 5/00; US 525/54.5; 527/500

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
US	106/273N; 525/54.5; 527/500

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
A	US, A; 2,716,616 PUBLISHED, 30 AUGUST 1955, RENDALL	1-10
A	US, A; 2,888,407 PUBLISHED, 26 MAY 1959, COOPER	1-10
A	US, A; 3,259,512 PUBLISHED, 5 JULY 1966, DICKSON	1-10
A	US, A; 3,303,151 PUBLISHED, 7 FEBRUARY 1967, PETERS	1-10
A	US, A; 3,513,005 PUBLISHED, 19 MAY 1970, BRADSHAW	1-10
A	US, A; 3,547,850 PUBLISHED, 15 DECEMBER 1970, MONTGOMERY	1-10
A	US, A; 3,997,354 PUBLISHED, 14 DECEMBER 1976, PIVETTE	1-10
A	US, A; 4,166,752 PUBLISHED, 4 SEPTEMBER 1979, MARZOCCHI	1-10

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
24 JANUARY 1983	07 FEB 1983
International Searching Authority [1]	Signature of Authorized Officer [20]
ISA/USA	THEODORE MORRIS

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	US, A; 4,273,588 PUBLISHED, 16 JUNE 1981, MARZOCCHI	1-10
A	US, A; 4,273,685 PUBLISHED, 16 JUNE 1981, MARZOCCHI	1-10
X P	US, A; 4,316,829 PUBLISHED, 23 FEB 1982 ROBERTS	1-10
X	JP, A; 49-52,287 PUBLISHED, 27 MAY 1974, NITIAN	1-10
X P	US, A; 4,333,866 PUBLISHED, 8 JUNE 1982, UFFNER	1-10

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [10]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers....., because they relate to subject matter [12] not required to be searched by this Authority, namely:

2. ☐ Claim numbers....., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [13], specifically:

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [11]

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.