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(54) Title: POLYMER-MODIFIED BITUMEN COMPOSITION

(57) Abstract: A polymer-modified bitumen composition is disclosed. The composition comprises bitumen, polymer and a compatibilising agent prepared by reacting one or more unsaturated monomers with a bituminous composition comprising asphaltenes and/or resins.



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POLYMER-MODIFIED BITUMEN COMPOSITION

Field of the Invention

The invention relates to a polymer-modified bitumen composition that is suitably used to prepare asphalt pavements. The invention further relates to a method for making the polymer-modified bitumen composition.

Background of the Invention

Bitumen is a viscous liquid or a solid consisting essentially of hydrocarbons and their derivatives. It is soluble in trichloroethylene and softens gradually when heated. Bitumen may be combined with aggregate to provide asphalt. The term "asphalt" in the present description is used to describe a mixture of bitumen and aggregate.

The physical properties of bitumen may be improved by blending a small quantity of polymer into the bitumen. In some instances, the polymer is not compatible with the bitumen, resulting in phase separation. One method of preventing incompatibility is to restrict the petroleum feedstocks that are used to produce the bitumen, using only feedstocks that are known to produce compatible bitumen. However, it is clearly preferable that the broadest range of feedstocks can be used to produce bitumen. Another method of preventing incompatibility is to use a compatibilising agent, i.e. an additional component that is added to the polymer/bitumen blend to enhance the compatibility of the polymer and the bitumen. US 5,719,216 discloses the use of bis(nitroaryl) disulphides and nitroaryl aryl disulphides as compatibilising agents.

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To avoid the problem of phase separation, chemically-modified bitumen wherein a polymer is chemically grafted onto the bitumen, has been prepared. It is believed that the polymer is bonded to asphaltene molecules, which typically constitute 5 to 25wt% of the bitumen. In US 4,301,051, bitumen is reacted with a polymerisable vinyl aromatic monomer and a rubbery polymer. It is suggested that the vinyl aromatic monomer couples the bitumen to the polymer by means of chemical bonds. In US 5,039,342, bitumen is chemically modified by reaction with a polymerisable ethylenically unsaturated monomer. By chemically bonding long polymeric chains onto asphaltene molecules it is possible to alter the physical properties of bitumen without encountering the phase separation problems experienced with physical blends of bitumen and polymer. However, chemically-modified bitumen differs from a physical blend of bitumen and polymer in that the interaction between the polymer chains and the bitumen is irreversible for the chemically-modified bitumen but reversible for the physical blend. With the physical blend, there is considerable interaction at typical road temperatures (up to 70°C), providing useful elasticity, but there is less interaction at road preparation temperatures (e.g. above 120°C), providing relatively low viscosity. By contrast, with a chemical interaction there may be high viscosity at high temperatures or poor elasticity at lower temperatures.

The present inventors have sought to provide a polymer-modified bitumen composition that is not subject to phase separation, preferably without restriction of the petroleum feedstock used to prepare the bitumen. The bitumen should preferably have physical properties such

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that it is suitable for use in the preparation of asphalt pavements. Additionally, the inventors have sought to use less polymer to achieve the same alteration in physical properties as achieved in known polymer-modified bitumen compositions. The inventors have also sought to provide polymer-modified bitumen having improved adhesion to aggregate and/or polymer-modified bitumen having improved rheological properties.

Summary of the Invention

Accordingly, the present invention provides a polymer-modified bitumen composition comprising:

- (a) bitumen,
- (b) polymer, and
- (c) a compatibilising agent prepared by reacting one or more unsaturated monomers with a bituminous composition comprising asphaltenes and/or resins.

The present invention further provides a method of preparing a polymer-modified bitumen composition, comprising steps of:

- (a) preparing a compatibilising agent by reacting one or more unsaturated monomers with a bituminous composition comprising asphaltenes and or/resins; and
- (b) blending the compatibilising agent with bitumen and with polymer.

The present inventors have prepared a compatibilising agent by reacting an unsaturated monomer with a bituminous composition comprising asphaltenes and/or resins. Asphaltenes and resins are two of four broad component groups found in bitumen (the others are aromatics and saturates; resins, aromatics and saturates are collectively known as maltenes). Asphaltenes are *n*-heptane insoluble black or brown amorphous solids, and

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are generally considered to be highly polar and complex aromatic materials of fairly high molecular weight. Resins are soluble in *n*-heptane and are typically dark brown in colour, solid or semi-solid and polar. In one embodiment of the invention, the bituminous composition comprising asphaltenes and/or resins is a bituminous composition comprising all four components, i.e. resins, aromatics, saturates and asphaltenes. In another embodiment of the invention, the bituminous composition comprising asphaltenes and/or resins is a composition consisting solely of asphaltenes, a composition consisting of solely of asphaltenes and resins, or a composition consisting solely of resins. It is believed that the reaction provides "surfactant" type structures wherein a short polymer chain is chemically bonded to an asphaltene or a resin. It is thought that the surfactant structure consists of a bitumen-like moiety and a polymer-like moiety, and can therefore improve the interaction between the bitumen and the polymer in the polymer-modified bitumen. The polymer-modified bitumen compositions of the invention are essentially physical blends of bitumen, polymer and compatibilising agent wherein the compatibilising agent improves the interaction between the bitumen and the polymer. The compatibilising agent helps to avoid phase separation in the bitumen composition, and allows the use of smaller quantities of polymer to achieve desirable physical properties. Additionally the compatibilising agent may improve the rheological properties of the bitumen composition.

Because the compositions of the present invention are essentially physical blends of polymer and bitumen, they are unlike the compositions of US 4,301,951 and US

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5,039,342, wherein the polymer is chemically bonded to the bitumen. Instead of chemically bonding the polymer to the bitumen, the present invention uses small quantities of compatibilising agent wherein short polymer chains are bonded to bitumen components, to improve the compatibility in a polymer/bitumen blend. Because the compositions of the invention are physical blends, they have temperature-dependent reversible interaction between the polymer and the bitumen, influencing the temperature-dependence of the physical properties.

Detailed Description of the Invention

The bitumen in the polymer-bitumen composition may be a residue from the distillation of crude oil, a cracked residue, a naturally occurring bitumen or a blend of various bitumen types. Examples of bitumen that may be conveniently used in the present invention include distillation or "straight run" bitumen, precipitation bitumen, e.g. propane bitumen, oxidised or blown bitumen, naphthenic bitumen or mixtures thereof.

The quantity of bitumen in the polymer-modified bitumen composition varies depending on the proposed use of the polymer-modified bitumen composition. For most applications, the quantity of bitumen is preferably greater than 75wt%, more preferably greater than 85wt%. For paving applications the quantity of bitumen is even more preferably greater than 90wt% and most preferably greater than 95wt%. Bitumen is typically the least expensive component in the composition so it is desirable to maximise the quantity of bitumen. For the purposes of describing the quantity of bitumen in the composition, the compatibilising agent (which is prepared by reaction of unsaturated monomers and a bituminous composition) is not classed as bitumen and is not included when assessing

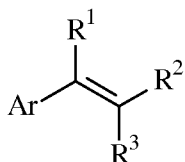
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the quantity of bitumen in the composition.

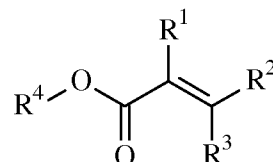
The polymer is preferably a thermoplastic elastomer or plastomer, more preferably a styrenic block copolymer, olefinic copolymer, polyurethane or polyether-polyester
5 copolymer. The styrenic block copolymers are most preferred and examples include styrene-butadiene-styrene (SBS) and styrene-isoprene-styrene (SIS). Another preferred polymer is ethylene vinyl acetate (EVA). More than one type of polymer may be incorporated in the
10 polymer-modified bitumen, e.g. a mixture of SBS and EVA, or a mixture of SIS and EVA. The quantity of polymer in the composition is preferably greater than 0.2wt%, more preferably greater than 0.5wt% and most preferably greater than 1wt%. The quantity of polymer in the
15 composition is preferably less than 25wt%, more preferably less than 20wt% and most preferably less than 15wt%. The quantity of polymer in the composition is preferably in the range 0.2 to 25wt% and more preferably in the range 0.5 to 20wt%. For paving applications the
20 quantity of polymer in the composition is preferably in the range 0.5 to 7wt%. The polymer is typically an expensive component, so it is desirable to incorporate the smallest quantity of polymer that achieves the required change in physical properties.

25 The compatibilising agent is prepared by reacting one or more unsaturated monomers with a bituminous composition comprising asphaltenes and/or resins. The one or more unsaturated monomers are preferably alkene or alkyne monomers, preferably one or more alkene monomers.
30 The one or more alkene monomers preferably includes at least one monomer of general formula A or B:

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A



B

wherein Ar is an aromatic group; R¹, R² and R³ are independently chosen from hydrogen and C₁₋₁₀ alkyl; and R⁴ is C₁₋₁₀ alkyl or an aromatic group. The aromatic group is typically phenyl, C₁₋₁₀ alkyl-substituted phenyl, halo-substituted phenyl, sulphate-substituted phenyl, sulphonate-substituted phenyl, naphthalene, C₁₋₁₀ alkyl-substituted naphthalene, halo-substituted naphthalene, sulphate-substituted naphthalene or sulphonate-substituted naphthalene and is preferably phenyl, tolyl, xylyl or chlorophenyl. R¹, R² and R³ are preferably hydrogen or methyl. R⁴ is preferably C₁₋₁₀ alkyl and is most preferably methyl, ethyl, propyl or butyl. Most preferably all of R¹, R² and R³ are hydrogen such that the alkenyl compound contains a terminal alkene and is a vinyl compound. Preferred alkenyl monomers of formula A (vinyl aromatic monomers) include styrene, *p*-chloro styrene, vinyl toluene, vinyl xylene, ethyl vinyl benzene and vinyl naphthalene. Preferred alkenyl monomers of formula B include methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, butyl acrylate and butyl methacrylate. The most preferred monomer is styrene.

In an alternative preferred embodiment of the invention, the one or more unsaturated monomers comprise a monomer of formula A or B and an acid anhydride monomer such as maleic anhydride monomer, more preferably a vinyl aromatic monomer of formula A and an acid anhydride monomer such as maleic anhydride monomer. Preferably the

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one or more unsaturated monomers are styrene and maleic anhydride. In this embodiment, the polymer chains attached to the asphaltenes and/or resins will result from copolymerisation of the vinyl aromatic monomer and the maleic anhydride monomer. The present inventors have observed that the inclusion of the maleic anhydride monomer improved the ability of the resulting polymer-modified bitumen composition to adhere to aggregate.

In one embodiment of the invention, the one or more unsaturated monomers are reacted with the bituminous composition comprising asphaltenes and/or resins in the presence of an initiator. Preferably, the reaction occurs in the presence of an initiator and a chain terminator. Suitable initiators include peroxide compounds such as benzoyl peroxide and azo compounds such as azobisisobutyronitrile (AIBN). Suitable chain terminators include alcohols such as isopropanol, ethers such as n-alkyl glycidyl ethers and ketones such as dialkyl ketones. The initiator can promote the reaction of the unsaturated monomers and the asphaltenes and/or resins. However, the inventors have observed that unsaturated monomers can react with the bituminous composition comprising asphaltenes and/or resins in the absence of initiator.

A bituminous composition comprising asphaltenes and/or resins is used to prepare the compatibilising agent. Bitumen (comprising the four broad groups of bitumen components: asphaltenes, resins, aromatics and saturates) may be used as the bituminous composition. Alternatively, bitumen may be separated into its components e.g. by filtration and precipitation, and a composition comprising asphaltenes and/or resins and optionally aromatics or saturates may be used as the

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bituminous composition. Preferably the bituminous composition comprises asphaltenes because it is considered that asphaltenes are most advantageously used to prepare the compatibilising agent.

5 The relative quantities of the bituminous composition and the one or more unsaturated monomers used in the preparation of the compatibilising agent determine the chain length of the polymer chains bonded to the asphaltenes and/or resins. Preferably the amount of one
10 or more unsaturated monomers is from 1 to 80wt% based upon the weight of the bitumen, more preferably from 1 to 20wt%.

 The reaction of one or more unsaturated monomers with the bituminous composition comprising asphaltenes
15 and/or resins may be carried out in air or may be carried out in an inert atmosphere, e.g. an argon atmosphere. The bituminous composition comprising asphaltenes and/or resins is preferably dissolved in a solvent. In a preferred embodiment of the invention, the one or more
20 unsaturated monomers act as the solvent. If an initiator and/or a chain terminator is used, it is dissolved in the solvent. In the most preferred embodiment, the one or more unsaturated monomers comprise styrene and styrene is used as the solvent. Preferably the reaction takes place
25 at a temperature of 100 to 200°C for a period of 1 to 12 hours.

 The compatibilising agent is blended with bitumen and with polymer. This may be carried out by high shear or low shear mixing of the three components, or may
30 alternatively be carried out by mixing in the presence of a solvent, with subsequent evaporation of the solvent. The solvent may be tetrahydrofuran (THF) or styrene.

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The quantity of compatibilising agent in the polymer-modified bitumen composition is preferably less than 25wt%, more preferably less than 20wt% and most preferably less than 15wt%. The quantity of the one or
5 more unsaturated monomers, expressed as a weight percentage of the polymer-modified bitumen composition is preferably less than 5wt%, more preferably less than 3wt%.

The polymer-modified bitumen composition may
10 comprise further additives, e.g. softening agents such as wax or penetration index boosters such as waxes, polyphosphoric acid and ethylene polymers.

The present invention further provides asphalt comprising a polymer-modified bitumen composition
15 according to the invention and aggregate. Asphalts are essentially mixtures of bitumen, as binder, with aggregate, in particular filler, sand and stones. There are many different types of asphalts available and their characteristics can vary quite significantly. The design
20 of asphalts for bituminous paving application is largely a matter of selecting and proportioning materials to obtain the desired properties in the finished construction.

Preferably stones comprise at least 10% of the
25 aggregate, more preferably at least 15% and most preferably at least 20%. Preferably stones comprise up to 70% of the aggregate, more preferably up to 65%, most preferably up to 60%. Filler and/or sand constitutes the balance.

30 The amount of the polymer-modified bitumen composition in the asphalt of the present invention will vary depending on the application for which the asphalt is to be used. However, the asphalt used in the present

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invention preferably comprises in the range of from 1 to 20% wt of the bitumen composition, more preferably in the range of from 2 to 10% wt, and most preferably in the range from 3 to 7% wt, based on total weight of asphalt.

5 The present invention further provides an asphalt pavement comprising asphalt according to the invention.

 The polymer-modified bitumen compositions of the invention can be used in conventional mix processes to form asphalt. The asphalt can be used to form asphalt
10 pavement in conventional pavement-laying processes. The asphalt may also be used in other processes such as waterproofing, roofing and pipe coating.

Examples

 The invention will now be described by reference to
15 examples which are not intended to be limiting of the invention.

Preparation of Compatibilising Agents

Compatibilising Agent 1

 524g of Bitumen S (Penetration 70dmm (EN1426) and
20 Softening Point 51°C (EN1427)) and 2.5g of dibenzoyl peroxide (Fluka 33581 97%, 25% water) were dissolved in 500g of styrene (Fluka 99%) in a two liter 3-neck round bottom flask at 80°C under continuous stirring. The solution was left to cool down to room temperature while
25 an argon flow was bubbled through the solution overnight under continuous stirring. The solution was then heated to 110°C for 3 hours after which the temperature was raised to 140°C for another 15 hours. Any residual styrene was removed by vacuum distillation at 160°C (3
30 hours). Yield (based on styrene conversion) 83%.

Compatibilising Agent 2

 The method used to prepare compatibilising agent 1 was repeated, except that the quantities of reagents were

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750g of Bitumen S, 405g of styrene and 2.5g of dibenzoyl peroxide, nitrogen instead of argon was bubbled through the solution, heating at 110°C was for 3.5 hours, heating at 140°C was for 19.5 hours and vacuum distillation at 160°C was for 21 hours. Yield (based on styrene conversion) 89%.

Compatibilising Agent 3

The method used to prepare compatibilising agent 2 was repeated, except that the quantities of reagents were 1000g of Bitumen S, 180g of styrene and 2.5g of dibenzoyl peroxide, heating at 140°C was for 20 hours and vacuum distillation at 160°C was for 11 hours. Yield (based on styrene conversion) 64%.

Compatibilising Agent 4

600g of Bitumen D (Penetration 72dmm (EN1426) and Softening Point 44.8°C (EN1427)) and 3g of dibenzoyl peroxide (Fluka 33581 97%, 25% water) were dissolved in 600g of styrene (Fluka 99%) in a two liter 3-neck round bottom flask. The contents were mixed and purged with nitrogen for 8 hours at 80°C. The temperature was raised to 110°C for 4 hours after which the temperature was raised to 140°C overnight. Any residual styrene was removed by vacuum distillation at 165°C.

Compatibilising Agent 5

25g of Bitumen D, 0.075g of dibenzoyl peroxide (Fluka 33581 97%, 25% water), 18g of styrene and 6g maleic anhydride were placed in in a 250ml 3-neck round bottom flask. The contents were mixed and purged with nitrogen for 30 minutes at 80°C. The temperature was raised to 110°C for 1 hour after which the temperature was raised to 140°C overnight. Any residual styrene was removed by vacuum distillation at 80°C. The weight ratio of styrene monomer: maleic anhydride monomer was 75:25.

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Compatibilising Agent 6

The method used to prepare compatibilising agent 5 was repeated, except that the quantities of styrene and maleic anhydride were altered such that the weight ratio of styrene monomer: maleic anhydride monomer was 50:50.

Compatibilising Agent 7

The method used to prepare compatibilising agent 5 was repeated, except that the quantities of styrene and maleic anhydride were altered such that the weight ratio of styrene monomer: maleic anhydride monomer was 90:10.

Compatibilising Agent 8

The method used to prepare compatibilising agent 5 was repeated, except that Bitumen S was used. The weight ratio of styrene monomer: maleic anhydride monomer was 75:25.

Compatibilising Agent 9

The method used to prepare compatibilising agent 7 was repeated, except that Bitumen S was used. The weight ratio of styrene monomer: maleic anhydride monomer was 90:10.

Compatibilising Agent 10

A sample of compatibilising agent 3 was further concentrated by dissolving in heptane under reflux conditions for 8 hours, and filtering off the resulting precipitate. The precipitate was subjected to a Soxhlet extraction with heptane, and was dried at 80°C in a vacuum oven for 8 hours.

Compatibilising Agent 11

960g of bitumen H2 (Penetration 80dmm (EN1426) and Softening Point 45.8°C (EN1427)) and 2.5g of dibenzoyl peroxide (Fluka 33581 97%, 25% water) were dissolved in 240g of styrene (Fluka 99%) in a two liter 3-neck round bottom flask at 80°C under continuous stirring. The

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solution was left to cool down to room temperature while an argon flow was bubbled through the solution overnight under continuous stirring. The solution was then heated to 110°C for 3 hours after which the temperature was
5 raised to 140°C for another 15 hours. Any residual styrene was removed by vacuum distillation at 160°C (3 hours).

Preparation of Polymer-Modified Bitumen

Polymer-modified bitumens were prepared by blending
10 bitumen, polymer and compatibilising agent. Blends as described in Table I were prepared:

Table I

	Bitumen	Polymer	Compatibilising Agent
Comparative Example 1	S	None	None
Comparative Example 2	S	5wt% SBS (Kraton D1101)	None
Comparative Example 3	S	4wt% SBS (Kraton D1101)	None
Comparative Example 4	S	3wt% SBS (Kraton D1101)	None
Example 1	S	4wt% SBS (Kraton D1101)	1wt% compatibilising agent 2
Comparative Example 5	D	None	None
Comparative Example 6	D	5wt% SBS (Kraton D1101)	None
Comparative Example 7	D	4wt% SBS (Kraton D1101)	None
Example 2	D	4wt% SBS (Kraton D1101)	1wt% compatibilising agent 6
Example 3	D	4wt% SBS (Kraton D1101)	1wt% compatibilising agent 5
Example 4	D	4wt% SBS (Kraton D1101)	1wt% compatibilising agent 2
Comparative Example 8	H1	3wt% SBS (Kraton D1101)	None
Example 5	H1	3wt% SBS (Kraton D1101)	0.1wt% compatibilising agent 10
Example 6	H1	3wt% SBS (Kraton D1101)	1.5wt% compatibilising agent 10
Comparative Example 9	H2	3wt% SBS (Kraton D1101)	None
Example 7	H2	3wt% SBS (Kraton D1101)	0.2wt% compatibilising agent 11
Example 8	H2	3wt% SBS (Kraton D1101)	2wt% compatibilising agent 11

Bitumen H1 has penetration 53dmm (EN1426) and Softening Point 50.0°C (EN1427).

Rheological Measurements

The phase angles (δ) at 300°C, 50°C and 70°C of the polymer-modified bitumen compositions were measured using an AR 2000 rheometer from TA instruments. The temperature sweep experiments were carried out with a fixed frequency of 10 rad/s, a conditioning time of 10s and a sampling time of 6s. The temperature range was from 25 to 80°C. The phase angle represents the phase difference between the stress and the strain. An ideal elastic material will have a δ of 0°; a purely viscous component will have a δ of 90°. Lower phase angle at low temperatures indicates more elastic behaviour at low temperatures (see Xioahu Lu, Polymer testing, 20 (2001) 77-86). The results are shown in Table II:

Table II

	$\delta(\pm 1\%)$ at 30°C	$\delta(\pm 1\%)$ at 50°C	$\delta(\pm 1\%)$ at 70°C
Comparative Example 1	70	83	Not recorded
Comparative Example 2	59	61	Not recorded
Comparative Example 3	60	67	Not recorded
Comparative Example 4	66	75	Not recorded
Example 1	53	63	Not recorded
Comparative Example 5	73	83	86
Comparative Example 6	61	62	87
Comparative Example 7	65	72	84
Example 2	58	62	Not recorded
Example 3	63	71	83
Example 4	Not recorded	70	83

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The inclusion of compatibilising agent 2 in example 1 lowers the phase angle at 30°C and 50°C when compared to a formulation with the same amount of SBS (comparative example 3) and lowers the phase angle at 30°C when compared to a formulation having 5wt% SBS (comparative example 2). The inclusion of compatibilising agent 6 in example 2 lowers the phase angle at 30°C and 50°C when compared to a formulation with the same amount of SBS (comparative example 7) and also lowers the phase angle at 30°C and 50°C when compared to a formulation having 5wt% SBS (comparative example 6). The inclusion of compatibilising agent 5 in example 3 and compatibilising agent 2 in example 4 lowers the phase angle at 70°C when compared to a formulation with 4wt% or 5wt% SBS (comparative examples 7 and 6).

Storage Stability

The storage stability of several polymer-modified bitumen examples was assessed by storing the blends in a "tootpath" vessel at 163°C for 2 days (ASTM D7173) and then measuring the ring and ball softening point at the top and the bottom of the vessel in order to determine the segregation between polymer and bitumen. The results are shown in table III:

Table III

	R&B top	R&B bottom	Δ R&B
Comparative Example 8	76.4	51	25.4
Example 5	57.2	53	4.2
Example 6	60.5	52.8	7.7
Comparative Example 9	95	54.8	40.6
Example 7	62	56.2	5.8
Example 8	59	56.2	2.8

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Examples 5 and 6 exhibit improved storage stability compared to comparative example 8. Examples 7 and 8 exhibit improved storage stability compared to comparative example 9.

5 Adhesion Measurements

Adhesion characteristics were measured by dissolving bitumen or compatibilising agent samples in dodecylbenzene at 0.1, 0.4, 1, 4 and 14wt% (dodecylbenzene is a high boiling solvent having properties comparable to maltenes). Three aggregates are placed on a glass plate and the dodecylbenzene solutions are applied such that all three aggregates are in contact with the solution. After 15 minutes, 1ml of 3wt% aqueous NaCl solution is added. The degree to which the aggregate is surrounded by the solution is determined after 10 minutes, 1 hour and 4 hours. If the proportion of solution surrounding the aggregate is between 0 and 25%, the adhesion is considered to be poor, between 26 and 50% is considered to be acceptable, between 51 and 75% is considered to be good and between 76 and 100% is considered to be excellent. The test was carried out for three different types of aggregate: basalt, gabbro and quartz. Table IV shows the results for basalt, Table V shows the results for gabbro and table VI shows the results for quartz.

Table IV

Sample	Conc.	10 minutes	1 hour	4 hours	Index	Adhesion
Comparison (Bitumen S)	0.1%	95	90	95	93	Excellent
	0.4%	100	100	100	100	Excellent
	1.0%	100	100	100	100	Excellent
	4.0%	100	100	100	100	Excellent
	14.0%	100	100	100	100	Excellent
Compatibilising agent 2	0.1%	75	65	65	68	Good
	0.4%	100	100	100	100	Excellent
	1.0%	100	100	100	100	Excellent
	4.0%	100	100	100	100	Excellent
	14.0%	100	100	100	100	Excellent
Compatibilising agent 9	0.1%	95	95	95	95	Excellent
	0.4%	95	95	90	93	Excellent
	1.0%	100	100	95	98	Excellent
	4.0%	100	100	100	100	Excellent
	14.0%	100	95	95	97	Excellent
Compatibilising agent 10	0.1%	90	85	70	82	Excellent
	0.4%	100	100	100	100	Excellent
	1.0%	100	100	100	100	Excellent
	4.0%	100	100	100	100	Excellent
	14.0%	100	100	100	100	Excellent
Comparison (Bitumen D)	0.1%	95	90	90	92	Excellent
	0.4%	95	90	95	93	Excellent
	1.0%	95	80	95	90	Excellent
	4.0%	100	85	100	95	Excellent
	14.0%	100	100	100	100	Excellent
Compatibilising agent 4	0.1%	95	80	90	88	Excellent
	0.4%	95	95	95	95	Excellent
	1.0%	95	95	95	95	Excellent
	4.0%	95	95	95	95	Excellent
	14.0%	100	100	100	100	Excellent
Compatibilising agent 7	0.1%	95	90	90	92	Excellent
	0.4%	95	95	95	95	Excellent
	1.0%	100	100	100	100	Excellent
	4.0%	100	100	100	100	Excellent
	14.0%	100	100	100	100	Excellent
Compatibilising agent 5	0.1%	95	95	90	93	Excellent
	0.4%	100	100	100	100	Excellent
	1.0%	100	100	100	100	Excellent
	4.0%	100	100	100	100	Excellent
	14.0%	100	100	100	100	Excellent

Table V

Sample	Conc.	10 minutes	1 hour	4 hours	Index	Adhesion
Comparison (Bitumen S)	0.1%	35	30	35	33	Acceptable
	0.4%	30	25	45	33	Acceptable
	1.0%	75	30	40	48	Acceptable
	4.0%	85	80	90	85	Excellent
	14.0%	95	90	95	93	Excellent
Compatibilising agent 2	0.1%	5	5	5	5	Poor
	0.4%	45	20	10	25	Acceptable
	1.0%	50	50	50	50	Good
	4.0%	95	90	90	92	Excellent
	14.0%	100	95	95	97	Excellent
Compatibilising agent 9	0.1%	75	70	65	70	Good
	0.4%	95	95	95	95	Excellent
	1.0%	95	95	95	95	Excellent
	4.0%	95	95	95	95	Excellent
	14.0%	100	100	100	100	Excellent
Compatibilising agent 10	0.1%	50	45	15	37	Acceptable
	0.4%	90	90	85	88	Excellent
	1.0%	90	90	90	90	Excellent
	4.0%	95	95	95	95	Excellent
	14.0%	100	100	100	100	Excellent
Comparison (Bitumen D)	0.1%	50	50	50	50	Good
	0.4%	50	50	45	48	Acceptable
	1.0%	90	75	85	83	Excellent
	4.0%	85	70	85	80	Excellent
	14.0%	70	95	60	75	Excellent
Compatibilising agent 4	0.1%	5	5	0	3	Poor
	0.4%	80	80	75	78	Excellent
	1.0%	90	60	65	72	Good
	4.0%	65	45	40	50	Good
	14.0%	100	95	95	97	Excellent
Compatibilising agent 7	0.1%	70	95	70	78	Excellent
	0.4%	90	85	85	87	Excellent
	1.0%	90	90	85	88	Excellent
	4.0%	95	95	95	95	Excellent
	14.0%	95	95	95	95	Excellent
Compatibilising agent 5	0.1%	80	80	75	78	Excellent
	0.4%	95	90	95	93	Excellent
	1.0%	95	100	100	98	Excellent
	4.0%	100	100	100	100	Excellent
	14.0%	100	100	100	100	Excellent

Table VI

Sample	Conc.	10 minutes	1 hour	4 hours	Index	Adhesion
Comparison (Bitumen S)	0.1%	90	75	95	87	Excellent
	0.4%	75	50	50	58	Good
	1.0%	95	90	90	92	Excellent
	4.0%	90	95	95	93	Excellent
	14.0%	95	95	95	95	Excellent
Compatibilising agent 2	0.1%	40	35	25	33	Acceptable
	0.4%	85	75	50	70	Good
	1.0%	100	100	100	100	Excellent
	4.0%	100	100	100	100	Excellent
	14.0%	100	100	100	100	Excellent
Compatibilising agent 9	0.1%	5	5	5	5	Poor
	0.4%	50	70	60	60	Good
	1.0%	55	35	25	38	Acceptable
	4.0%	60	55	60	58	Good
	14.0%	75	75	70	73	Good
Compatibilising agent 10	0.1%	5	5	5	5	Poor
	0.4%	80	65	75	73	Good
	1.0%	20	5	5	10	Poor
	4.0%	40	25	15	27	Acceptable
	14.0%	75	65	65	68	Good
Comparison (Bitumen D)	0.1%	5	5	5	5	Poor
	0.4%	80	85	70	78	Excellent
	1.0%	75	45	50	57	Good
	4.0%	70	50	50	57	Good
	14.0%	75	75	70	73	Good
Compatibilising agent 4	0.1%	70	65	70	68	Good
	0.4%	65	65	60	63	Good
	1.0%	85	85	80	83	Excellent
	4.0%	100	90	85	92	Excellent
	14.0%	70	85	90	82	Excellent
Compatibilising agent 7	0.1%	30	25	15	23	Poor
	0.4%	25	15	10	17	Poor
	1.0%	50	45	50	48	Acceptable
	4.0%	30	30	20	27	Acceptable
	14.0%	50	50	55	52	Good
Compatibilising agent 5	0.1%	75	70	65	70	Good
	0.4%	85	85	85	85	Excellent
	1.0%	50	45	50	48	Acceptable
	4.0%	100	100	100	100	Excellent
	14.0%	100	100	100	100	Excellent

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The adhesion of Bitumen S to basalt is excellent, and the adhesion observed with compatibilising agents based upon Bitumen S (compatibilising agents 2, 9 and 10) is also excellent. The adhesion of Bitumen D to basalt is also excellent, but the adhesion observed with the compatibilising agents based upon Bitumen D (compatibilising agents 4, 5 and 7) is superior.

The adhesion of Bitumen S and Bitumen D to gabbro ranges from acceptable to excellent, depending upon the concentration of the bitumen in the dodecylbenzene solution. The adhesion observed with the compatibilising agents is similar for the bitumen-styrene compatibilising agents (2 and 4), but is markedly better for the bitumen-styrene-maleic anhydride compatibilising agents (5, 7, 9 and 10).

The adhesion of Bitumen S to quartz ranges from good to excellent. The adhesion observed with the bitumen-styrene compatibilising agent (2) is slightly better, but the adhesion observed the bitumen-styrene-maleic anhydride compatibilising agent is slightly worse (9 and 10). The adhesion of Bitumen D to quartz ranges from poor to excellent, depending upon the concentration of the bitumen in the dodecylbenzene solution. The adhesion is improved with compatibilising agents 4 and 5, but is worse with compatibilising agent 7 (having a 90:10 styrene: maleic anhydride ratio). With compatibilising agent 5 (having a 75:25 styrene: maleic anhydride ratio) the adhesion is superior for most bitumen concentrations in dodecylbenzene.

The adhesion measurements simulate rainy weather conditions during road construction. If the asphalt becomes wet within a few days after completion of the road, there may not have been sufficient time for

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effective adhesion to have developed between the aggregate and bitumen. It is desirable, particularly when constructing roads in countries where rain is a regular occurrence, to ensure that effective adhesion
5 develops in a short period of time. The results above show that the compatibilising agents can be used to improve the adhesion between polymer-modified bitumen and aggregate.

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C L A I M S

1. A polymer-modified bitumen composition comprising:
 - (a) bitumen,
 - (b) polymer, and
 - (c) a compatibilising agent prepared by reacting one or
5 more unsaturated monomers with a bituminous
composition comprising asphaltenes and/or resins.
2. A polymer-modified bitumen composition according to
claim 1, wherein the polymer is a styrenic block
copolymer, olefinic copolymer, polyurethane or polyether-
10 polyester copolymer or mixtures thereof.
3. A polymer-modified bitumen composition according to
claim 1 or claim 2, wherein the one or more unsaturated
monomers are one or more alkene monomers and/or one or
more alkyne monomers.
- 15 4. A polymer-modified bitumen composition according to
claim 3, wherein the one or more alkene monomers includes
at least one vinyl aromatic monomer.
5. A polymer-modified bitumen composition according to
claim 4, wherein the at least one vinyl aromatic monomer
20 is styrene.
6. A polymer-modified bitumen composition according to
claim 3, wherein the one or more alkene monomers comprise
a vinyl aromatic monomer and maleic anhydride monomer.
7. A polymer-modified bitumen composition according to
25 any preceding claim, wherein the one or more unsaturated
monomers are reacted with the bituminous composition
comprising asphaltenes and/or resins in the presence of
an initiator.

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8. A polymer-modified bitumen composition according to any preceding claim, wherein the quantity of compatibilising agent is less than 20wt%.

5 9. A method of preparing a polymer-modified bitumen composition, comprising steps of:

(a) preparing a compatibilising agent by reacting one or more unsaturated monomers with a bituminous composition comprising asphaltenes and/or resins; and

10 (b) blending the compatibilising agent with bitumen and with polymer.

10. Asphalt comprising a polymer-modified bitumen composition according to any one of claims 1 to 8 and aggregate.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2008/059713

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08L95/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08L C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 301 051 A (MARZOCCHI ALFRED ET AL) 17 November 1981 (1981-11-17) cited in the application claims 1-14	1-10
Y	-----	1-10
X	US 5 039 342 A (JELLING MURRAY [US]) 13 August 1991 (1991-08-13) cited in the application claims 1-14	1-10
Y	-----	1-10
Y	US 3 146 118 A (THORPE ROY E) 25 August 1964 (1964-08-25) claims 1,2; table II ----- -/--	1-10



Further documents are listed in the continuation of Box C:



See patent family annex.

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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2008/059713

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 4 554 022 A (GROSSI ANTHONY V [US] ET AL) 19 November 1985 (1985-11-19) claims 1-10	1-10
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Y	-----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2008/059713

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US 5039342	A	13-08-1991	NONE	
US 3146118	A	25-08-1964	NONE	
US 4378447	A	29-03-1983	NONE	
US 4554022	A	19-11-1985	NONE	
US 4518741	A	21-05-1985	NONE	