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(54) Title: BITUMINOUS COMPOSITION

(57) Abstract: The present invention relates to a bituminous composition comprising from 20 wt% to 99.9 wt% of bitumen and from 0.01 wt% to 10 wt% of an aminic compound selected from carbamides, thiocarbamides, carbamates and thiocarbamates, and mixtures thereof. The present invention also relates to an asphalt composition comprising said bituminous composition and filler and/or aggregate. The bituminous and asphalt compositions of the present invention exhibit significantly reduced H₂S emissions.



WO 2012/004199 A1

BITUMINOUS COMPOSITION

Field of the Invention

The invention relates to a bituminous composition and asphalt compositions comprising said bituminous composition. The invention further relates to a process for the manufacture of a bituminous composition and a process for the manufacture of an asphalt composition.

Background of the Invention

In the road construction and road paving industry, it is a well-practised procedure to coat aggregate material such as sand, gravel, crushed stone or mixtures thereof with hot fluid bitumen, spread the coated material as a uniform layer on a road bed or previously built road while it is still hot, and compact the uniform layer by rolling with heavy rollers to form a smooth surfaced road.

The combination of bitumen with aggregate material, such as sand, gravel, crushed stone or mixtures thereof, is also referred to as "asphalt". Bitumen, also referred to as "asphalt binder", is usually a liquid binder comprising asphaltenes, resins and solvents. Bitumen can for example comprise pyrogenous mixtures derived from petroleum residues such as residual oils, tar or pitch or mixtures thereof.

It is known in the art that sulphur can be mixed with bitumen for applications in the road construction and road paving industry. Sulphur-modified bitumen is formulated by replacing some of the bitumen in conventional binders by elemental sulphur.

One of the problems encountered when using sulphur in bitumen is the unwanted formation of H₂S, resulting

from dehydrogenation reactions between bitumen and sulphur at high temperatures.

Even low $\frac{3}{4}$ S emission from sulphur-comprising asphalt, meaning asphalt formulated using sulphur-modified bitumen wherein elemental sulphur has been used to replace part of the bitumen, presents an emission nuisance on road paving projects. This is due to the gradual H_2S gas concentration increase to high levels in the air voids in the loose paving mixture during storage in silos and during truck delivery to the paving site. The "stored" gas is released when the air pockets in the mixture are opened up as the mixture is dumped from the delivery trucks or as the mixture is subjected to mechanical mixing.

In view of the substantial amounts of sulphur used, especially in sulphur-containing asphalt having high sulphur-bitumen weight ratios, e.g. as high as 1:1, H_2S emission is a serious problem. Therefore, it is necessary to reduce the unwanted formation and emission of H_2S from sulphur-comprising asphalt.

Since bitumen inherently contains low levels of sulphur, emission of $\frac{3}{4}$ S is even a problem for bitumen and asphalt compositions which have not been modified with additional sulphur.

Various attempts have been made to reduce $\frac{3}{4}$ S emissions from sulphur-modified bitumen and asphalt compositions. However, further improvements are needed.

Summary of the Invention

It has now been found that significantly reduced $\frac{3}{4}$ S emissions can be achieved by incorporating selected aminic compounds into bituminous and asphalt compositions .

Hence according to the present invention there is provided a bituminous composition comprising from 20 wt% to 99.9 wt% of bitumen and from 0.01 wt% to 10 wt% of an aminic compound selected from carbamides, thiocarbamides , carbamates and thiocarbamates , and mixtures thereof. All weight percentages herein are by weight of the bituminous composition unless otherwise specified.

According to another aspect of the present invention there is provided an asphalt composition comprising the bitumen composition as claimed herein and filler and/or aggregate .

According to another aspect of the present invention there is provided a process for manufacturing the bituminous composition according to the present invention, the process comprising the steps of:

- (i) heating bitumen;
- (ii) optionally mixing the hot bitumen so obtained with an amount of sulphur in the range of from 0.5 wt% to 75 wt%;

wherein from 0.01 wt% to 10 wt% of an aminic compound is added in at least one of the steps (i) or (ii), all weight% being by weight of the bituminous composition.

According to yet another aspect of the present invention there is provided a process for manufacturing the asphalt composition according to the present invention, the process comprising the steps of:

- (i) heating bitumen;
- (ii) heating aggregate;
- (iii) mixing the hot bitumen with the hot aggregate in a mixing unit to form an asphalt composition;

optionally wherein from 0.5 wt% to 75 wt% of sulphur, is added in at least one of steps (i), (ii) or (iii); and wherein from 0.01 wt% to 10 wt% of aminic compound, is

added in at least one of the steps (i), (ii) or (iii), all weight% being by weight of the bituminous composition comprising bitumen, aminic compound, and optionally sulphur .

5 According to yet another aspect of the present invention there is provided the use of an aminic compound selected from carbamides, thiocarbamides , carbamates, thiocarbamates , and mixtures thereof, for reducing H₂S emissions from a bituminous composition wherein the
10 bituminous composition comprises from 20 wt% to 99.9 wt% of bitumen and from 0.01 wt% to 10 wt% of an aminic compound selected from carbamides, thiocarbamides, carbamates and thiocarbamates, and mixtures thereof.

Detailed Description of the Invention

15 A first essential component of the bituminous composition herein is bitumen. The bitumen can be selected from a wide range of bituminous compounds. Whereas some documents in the prior art prescribe that the bitumen must have been subjected to blowing before it
20 is to be used in paving applications, such requirement is not needed in the compositions according to the present invention. so, bitumen that can be employed may be straight run bitumen, thermally cracked residue or precipitation bitumen, e.g., from propane. Although not
25 necessary, the bitumen may also have be subjected to blowing. The blowing may be carried out by treating the bitumen with an oxygen-containing gas, such as air, oxygen-enriched air, pure oxygen or any other gas that comprises molecular oxygen and an inert gas, such carbon
30 dioxide or nitrogen. The blowing operation may be conducted at temperatures of 175 to 400°C, preferably from 200 to 350°C. Alternatively, the blowing treatment may be conducted by means of a catalytic process.

Suitable catalysts in such processes include ferric chloride, phosphoric acid, phosphorus pentoxide, aluminium chloride and boric acid. The use of phosphoric acid is preferred.

5 The bitumen for use herein is preferably a paving grade bitumen suitable for road application having a penetration of, for example, from 9 to 1000dmm, more preferably of from 15 to 450dmm (tested at 25°C according to EN 1426: 1999) and a softening point of from 25 to
10 100°C, more preferably of from 25 to 60°C (tested according to EN 1427: 1999).

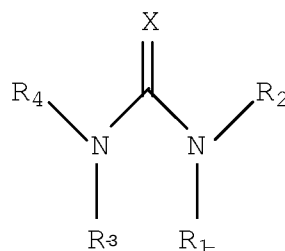
 The bitumen content in the bitumen composition according to the invention may range from 20 to 90%wt, based on the weight of the bituminous composition. Good
15 results have been obtained with amounts ranging from 50 to 75 %wt.

 A second essential component of the bituminous composition herein is an aminic compound selected from carbamides, thiocarbamides, carbamates, and
20 thiocarbamates, and mixtures thereof.

 The aminic compound is present at a level in the range of from 0.01 wt% to 10 wt%, preferably in the range of 0.1 wt% to 5 wt%, more preferably in the range of 0.2 wt% to 3.5 wt%, all percentages being by weight of the
25 bituminous composition.

 The carbamides and thiocarbamides are preferably selected from compounds of formula I:

- 6 -



(I)

wherein X is O or S and wherein R¹ to R⁴ are each individually selected from hydrogen and ci-cis hydrocarbyl groups optionally substituted with one or more functional groups .

5 The ci-cis hydrocarbyl groups are preferably selected from ci-cis aliphatic hydrocarbyl groups, c₃-c₁₈ alicyclic hydrocarbyl groups and c₃-c₁₈ aromatic hydrocarbyl groups. The c₁-c₁₈ hydrocarbyl groups in formula (I) are more preferably selected from c₁-c₆ alkyl, phenyl and benzyl, especially methyl, ethyl, propyl, butyl, phenyl and benzyl .

10 The c₁-c₁₈ hydrocarbyl groups may be optionally substituted with one or more functional groups. Suitable functional groups include amino, alkoxy, amine ethoxylates, olefinic, alcohol ethoxylates, carbonyl, carboxy esters, amides, silyl ethers, thiols and thio ethers. Examples of suitable functional groups include -NH₂, -N(CH₂CH₂O)_mH(CH₂CH₂O)_nH wherein n and m is 1 to 15, -O(CH₂CH₂O)_nH wherein n is 1-15, -OH, -OR wherein R is methyl, ethyl or propyl, -COOH, -COOR wherein R is methyl, ethyl or propyl, and -Si(OR)₃ wherein R is methyl, ethyl or propyl.

20 Examples of suitable substitution patterns for the carbamide and thiocarbamide compounds of formula (I) are as follows:

- (i) one of the R¹-R⁴ groups is a ci-cis hydrocarbyl optionally substituted with one or more functional

groups and three of the R^1 - R^4 groups are hydrogen (i.e. monosubstituted carbamide or monosubstituted thiocarbamide);

(ii) one of the R^1 - R^2 groups is a *ci-cis* hydrocarbyl group optionally substituted with one or more functional groups and the other of the R^4 - R^2 groups is hydrogen and one of the R^3 - R^4 groups is a *ci-cis* hydrocarbyl group optionally substituted with one or more functional groups and the other of the R^3 - R^4 groups is hydrogen (i.e. 1,3-disubstituted carbamide or 1,3-disubstituted thiocarbamide);

(iii) both of the R^4 - R^2 groups (or both of the R^3 - R^4 groups) are a *ci-cis* hydrocarbyl group optionally substituted with one or more functional groups and both of R^3 - R^4 groups (or both of the R^4 - R^2 groups) are hydrogen (i.e. 1,1-disubstituted carbamide or 1,1-disubstituted thiocarbamide);

(iv) one of the R^4 - R^4 groups is hydrogen and the other three R^4 - R^4 groups are each individually selected from a *ci-cis* hydrocarbyl group optionally substituted with one or more functional groups (i.e. a trisubstituted carbamide or a trisubstituted thiocarbamide);

(v) all of the R^4 - R^4 groups are each individually selected from a *ci-cis* hydrocarbyl group optionally substituted with one or more functional groups (i.e. a tetrasubstituted carbamide or a tetrasubstituted thiocarbamide);

(vi) all of the R^4 - R^4 groups are hydrogen (i.e. carbamide or thiocarbamide).

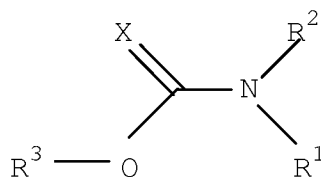
In a preferred embodiment of the present invention, all of the R^4 - R^4 groups are hydrogen.

In another preferred embodiment of the present invention the X group of formula (I) is O (i.e. carbamide or substituted carbamide) .

Examples of suitable carbamide compounds for use in the present invention include urea, N,N'-(bishydroxymethyl)urea, N,N'-dimethyl urea, N,N'-trimethyl urea, 1,1-dimethyl urea, 1,3-diethyl urea, 1,3-dimethyl-1,3-diphenyl urea, benzyl urea, tert-butyl urea, phenyl urea, 1,3-diphenyl urea, 1,3-carbonyl dipiperidine, 1,3-dipropyl urea, 1,3-dibutyl urea and l-[3-(trimethoxysilyl)propyl]urea .

A particular preferred carbamide compound for use in the present invention is urea.

The carbamates and thiocarbamates are preferably selected from compounds of formula II:



(II)

wherein X is O or S and wherein R¹ to R³ are each individually selected from hydrogen and ci-cig hydrocarbyl groups optionally substituted with one or more functional groups .

The ci-cig hydrocarbyl groups in formula (II) are preferably selected from ci-cig aliphatic hydrocarbyl groups, C₃-C₁₈ alicyclic hydrocarbyl groups and C₃-C₁₈ aromatic hydrocarbyl groups. The ci-cig hydrocarbyl groups in formula (II) are more preferably selected from C₁-C₆ alkyl, phenyl, benzyl, especially methyl, ethyl, propyl, butyl and phenyl .

The ci-cig hydrocarbyl groups in formula (II) may be optionally substituted with one or more functional groups. Suitable functional groups include amino, alkoxy,

amine ethoxylates, olefinic, alcohol ethoxylates, carbonyl, carboxy esters, amides, silyl ethers, thiols and thio ethers. Examples of suitable functional groups include $-NH_2$, $-N(CH_2CH_2O)_mH(CH_2CH_2O)_nH$ wherein n and m is 1 to 15, $-O(CH_2CH_2O)_nH$ wherein n is 1-15, $-OH$, $-OR$ wherein R is methyl, ethyl or propyl, $-COOH$, $-COOR$ wherein R is methyl, ethyl or propyl, and $-Si(OR)_3$ wherein R is methyl, ethyl or propyl.

Both O -substituted and N -substituted carbamates of formula (II) are suitable for use in the bituminous composition herein.

In a preferred embodiment of the present invention, all of the R^1 - R^3 groups are hydrogen.

In another preferred embodiment of the present invention the X group of formula (I) is O (i.e. carbamate or substituted carbamate).

Examples of suitable carbamate compounds for use in the present invention include methyl carbamate, ethyl carbamate (also known as urethane), tert-butyl carbamate, phenyl carbamate and propyl carbamate.

Sulphur constitutes a highly preferred part of the binder material herein. Preferably, substantial amounts of sulphur are used in the bituminous composition of the present invention as a binder, however smaller amounts of sulphur (e.g. 0.5-2 wt% where sulphur is used as a cross-linking agent) can also be employed. In the composition of the present invention the sulphur is preferably present in amounts ranging from 0.5 to 75 %wt, more preferably from 5 to 75%wt, based on the weight of the bituminous composition. Suitably, sulphur may be present in the bitumen composition in amounts ranging from 20 to 60%wt, since the strength enhancement that is being provided to the bitumen composition by the sulphur is

reduced when less than 20%wt of sulphur is being used in the bitumen composition according to the invention.

As described in WO-A 03/014231 the sulphur may be added to the bitumen composition in the form of sulphur pellets, and preferably, the sulphur is incorporated into the compositions of the present invention in this form. Reference herein to pellets is to any type of sulphur material that has been cast from the molten state into some kind of regularly sized particle, for example flakes, slates or sphere-shaped sulphur such as prills, granules, nuggets and pastilles or half pea sized sulphur. The sulphur pellets typically comprise from 50 to 100wt% of sulphur, based upon the weight of the sulphur pellets, preferably from 60wt% and most preferably from 70wt%; and typically to 99wt%, and preferably to 95wt% or to 100wt%. A more preferred range is from 60 to 100wt%.

These pellets may contain carbon black and, optionally, other ingredients, such as amyl acetate and wax. Carbon black may be present in amounts up to 5%wt, based on the pellet, preferably up to 2%wt. Suitably, the content of carbon black in the sulphur pellet is at least 0.25wt. The content of other ingredients, such as amyl acetate and wax, typically does not exceed an amount of 1.0%wt each. When wax is present, it may be in the form of, for example, slack wax or wax derived from a Fischer-Tropsch process. Examples of suitable waxes for use herein are Sasobit (RTM), a Fischer-Tropsch derived wax commercially available from Sasol, and SX100 wax, a Fischer-Tropsch wax from Shell Malaysia.

In one embodiment of the present invention, the aminic compound is present in the sulphur pellet.

An example of a suitable sulphur pellet for use herein is Thiopave (RTM) pellets commercially available from Shell Canada.

Whereas the bituminous composition according to the invention comprises the two essential components, bitumen and aminic compound, and also preferably sulphur, it is evident to the skilled person that to such a composition also different compounds may be added.

For instance, the bituminous composition herein may comprise one or more polymers. Suitable polymers for use herein include those disclosed in WO-A 03/014231. Examples of suitable polymers for use herein include, but are not limited to, styrene butadiene rubber and a styrene-butadiene-styrene block copolymer.

The bituminous composition according to the present invention may also comprise an odour suppressant.

The bituminous and asphalt compositions of the present invention may also comprise wax, for example, slack wax or wax derived from a Fischer-Tropsch process. Examples of suitable waxes for use herein are Sasobit (RTM), a Fischer-Tropsch derived wax commercially available from Sasol, and SX100 wax, a Fischer-Tropsch wax from Shell Malaysia.

The bituminous and asphalt compositions of the present invention may also comprise warm mix asphalt additives. Examples of suitable additives include, but are not limited to, Evotherm 3G commercially available from MeadWestvaco and Rediset WMX commercially available from Akzo Nobel.

The bituminous and asphalt compositions of the present invention may also comprise anti-stripping agents .

The bituminous and asphalt compositions of the present invention may also comprise ethylene bisstearamide such as disclosed in WO 2009/121913.

5 The bitumen composition according to the invention is advantageously used in the form of an asphalt composition comprising the bitumen composition and filler and/or aggregate. Examples of fillers have been described in US-A 5863971, and include carbon black, silica, calcium carbonate, stabilisers, antioxidants, pigments
10 and solvents. Examples of aggregates include sand, rock, gravel, stones, pebbles etc. These aggregate materials are particularly useful for paving roads.

Typically, the asphalt composition comprises at least 1 wt% of bitumen, based on the weight of the asphalt composition. An asphalt composition comprising
15 from about 1 weight% to about 10 weight% of bitumen is preferred, with a special preference for asphalt compositions comprising from about 3 weight % to about 7 weight % of bitumen, based on the weight of the asphalt composition.
20

The bituminous composition according to the present invention can be prepared by mixing bitumen, aminic compound and preferably sulphur in the appropriate amounts .

25 Accordingly, the present invention provides a process for manufacturing the bituminous composition according to the present invention, the process comprising the steps of:

- (i) heating bitumen;
- 30 (ii) optionally mixing the hot bitumen so obtained with an amount of sulphur in the range of from 0.5 wt% to 75 wt%;

wherein from 0.01 wt% to 10 wt% of an aminic compound is added in at least one of the steps (i) or (ii), all weight% being by weight of the bituminous composition.

According to another aspect of the present invention there is provided a process for manufacturing a bituminous composition comprising the steps of:

- (i) heating a preblend of bitumen and aminic compound wherein the level of aminic compound is in the range of from 0.01 wt% to 10 wt%, by weight of the bituminous composition;
- (ii) optionally mixing the heated preblend of bitumen and aminic compound with an amount of sulphur in the range of from 0.5 wt% to 75 wt%, by weight of the bituminous composition.

In the processes of the present invention, the aminic compound may be added in molten form or in the form of granules or in solution.

The present invention also provides a process for manufacturing the asphalt composition according to the present invention, the process comprising the steps of:

- (i) heating bitumen;
- (ii) heating aggregate;
- (iii) mixing the hot bitumen with the hot aggregate in a mixing unit to form an asphalt composition; optionally wherein from 0.5 wt% to 75 wt% of sulphur, is added in at least one of steps (i), (ii) or (iii); and wherein from 0.01 wt% to 10 wt% of aminic compound, is added in at least one of the steps (i), (ii) or (iii), all weight% being by weight of the bituminous composition comprising bitumen, aminic compound, and optionally sulphur.

The present invention also provides a process for manufacturing the asphalt composition according to the present invention, the process comprising the steps of:

- (i) heating a preblend of bitumen and aminic compound wherein the level of aminic compound is in the range of from 0.01 wt% to 10 wt%;
- (ii) heating aggregate;
- (iii) mixing the hot preblend of bitumen and aminic compound with the hot aggregate in a mixing unit to form an asphalt composition; optionally wherein from 0.5 wt% to 75 wt% of sulphur, is added in at least one of steps (i), (ii) or (iii); all weight% being by weight of the bituminous composition.

In step (i) of the processes for manufacturing the present bituminous or asphalt compositions the bitumen (or preblend of bitumen and aminic compound) is heated, preferably at a temperature of from 60°C to 200°C, preferably from 80 to 150°C, more preferably from 100°C to 145°C, and even more preferably from 125°C to 145°C. Working above 120 °C has the advantage that sulphur is liquid which facilitates the mixing process. Although the skilled person can easily determine the optimal mixing time the mixing time may be relatively short, e.g., from 10 to 600 seconds.

In step (ii) of the process for manufacturing the present asphalt composition the aggregate is heated, preferably at a temperature of from 60 to 200°C, preferably from 80 to 170°C, more preferably from 100 to 160°C, even more preferably from 100 to 145°C. The aggregate is suitably any aggregate that is suitable for road applications. The aggregate may consist of a mixture of coarse aggregate (retained on a 4mm sieve), fine

aggregate (passes a 4mm sieve but is retained on a 63 μ m sieve) and filler (passes a 63 μ m sieve).

In step (iii) of the asphalt manufacturing process, the hot bitumen (or hot preblend of bitumen and aminic compound) and hot aggregate are mixed in a mixing unit. Suitably, the mixing takes place at a temperature of from 80 to 200°C, preferably from 90 to 150°C, more preferably from 100 to 145°C. Typically, the mixing time is from 10 to 60 seconds, preferably from 20 to 40 seconds.

The temperatures at which the bitumen and aggregate are heated and subsequently mixed are desirably kept as low as possible in order to reduce hydrogen sulphide emissions when the sulphur is added. However, the temperatures need to be sufficiently high such that the bitumen can effectively coat the aggregate. The present invention allows for bitumen, aggregate and sulphur mixes to be produced with suppression of H₂S emanating from the asphalt mixture.

In the process of manufacturing asphalt, sulphur, when present, is preferably added as late as possible in the process, preferably in step (iii).

In the processes of the present invention, it is preferable to add sulphur in the form of sulphur pellets, as described above.

The sulphur and the aminic compound may be added together, i.e. both in step (i), step (ii) or step (iii) of the respective processes for manufacturing the present bituminous and asphalt compositions. In a first embodiment, the hot aggregate is mixed with the sulphur, when present, and the aminic compound. Hot bitumen is then added to the hot aggregate- (sulphur)-aminic compound mixture. In a second embodiment, hot aggregate is mixed with hot bitumen, and the sulphur, when present, and the

aminic compound are added to the hot bitumen-aggregate mixture. This embodiment offers the advantage of producing a stronger sulphur-asphalt mixture strength. In a third embodiment, hot bitumen is mixed with sulphur, when present, and the aminic compound and the resulting hot bitumen-sulphur-aminic compound mixture is mixed with hot aggregate to obtain a sulphur-comprising asphalt mixture .

Alternatively, in the asphalt manufacture process the aminic compound may be added separately. For example, the aminic compound may be added to the bitumen in step (i) and the sulphur may be added in step (iii) .

In one embodiment of the invention, the sulphur and the aminic compound are added together; the sulphur is in the form of pellets and the aminic compound is incorporated in the sulphur pellets. The sulphur pellets preferably comprise from 0.01 to 10 wt% of the aminic compound, based upon the weight of the bituminous composition. The sulphur pellets are suitably prepared by a process wherein liquid sulphur is mixed with the aminic compound and optionally additional components such as carbon black, amyl acetate and any suitable emulsifying agent. The mixture is then shaped and/or pelletised.

In one embodiment of the invention sulphur may be added in the form of two types of sulphur pellets; a first type of sulphur pellet that comprises the aminic compound and a second type of sulphur pellet that does not comprise the aminic compound. This has the advantage that the aminic compound is essentially concentrated in the first type of sulphur pellet and conventional sulphur pellets can be used to make up the rest of the sulphur requirement .

The invention further provides a process for preparing an asphalt pavement, wherein asphalt is prepared by a process according to the invention, and further comprising steps of:

- (iv) spreading the asphalt into a layer; and
- (v) compacting the layer.

The invention further provides an asphalt pavement prepared by the processes according to the invention.

The compaction in step (v) suitably takes place at a temperature of from 80 to 200°C, preferably from 90 to 150°C, more preferably from 100 to 145°C. The temperature of compaction is desirably kept as low as possible in order to reduce hydrogen sulphide emissions. However, the temperature of compaction needs to be sufficiently high such that the voids content of the resulting asphalt is sufficiently low for the asphalt to be durable and water resistant .

The invention will now be described by reference to examples which are illustrated by means of the following Examples, which are not intended to limit the invention.

Examples

Bituminous compositions were prepared according to the following procedure. Bitumen was pre-heated in an oven for 2 hours at 160°C. 24.4 g of this pre-heated bitumen was placed in a 3 neck round bottom flask followed by addition of 16.2 g of elemental sulphur pellets (supplied as Thiopave pellets from Shell Canada containing 99 wt% sulphur and 1 wt% carbon black) while maintaining stirring rate at 1000 rpm. To test the effect of urea/urea derivative on H₂S emissions, 0.77 g of urea or 1- [3-trimethoxysilyl]propyl]urea urea derivative was added to the above mix which was maintained at 140 °C and the stirring was continued for a further 4 minutes. A

Drager "Multiwarn" $\frac{3}{4}$ S gas detector was connected to one of the necks of the round bottom flask containing the blend sample which was maintained at 140 °C under continuous 275 rpm stirring rate. $\frac{3}{4}$ S emissions were measured. The results are shown in Table 1 below.

Table 1

	Urea (g)	1-[3-trimethoxysilyl propyl]urea (g)	Temperature, (°C)	H ₂ S (ppm)
Comparative Example 1	0	0	140	40
Example 2	0	0.77	140	10
Example 3	0.77	0	140	1
Comparative Example 4	0	0	160	75
Example 5	0.77	0	160	18
Comparative Example 6	0	0	170	>100
Example 7	0.77	0	170	35

Asphalt mixes were made according to the following procedure. 1543 g of aggregates were heated for a period of 5 hours in a hot air oven at a temperature of 140°C, 150°C or 160°C. The exact temperature (i.e. 140°C, 150°C and 160°C) corresponded to the temperature at which the urea or urea derivative was being evaluated at (see results Table 2). The heated aggregates were mixed with 48.7 g of hot bitumen (penetration grade 80/100) for 1 minute followed by the addition of 32.5 g elemental sulphur pellets (in the form of Thiopave pellets commercially available from Shell Canada containing 99 wt% sulphur and 1 wt% carbon black). Mixing was continued for a further 4 minutes. When present, the urea or urea

derivative in an amount indicated in Table 2 was added 10 seconds after the addition of the elemental sulphur pellets. In one of the experiments, urea was added along with the hot bitumen (Example 16). After a total of 5 minutes of mixing the asphalt mix was transferred into an insulated 5-liter vessel. The vessel was covered with a lid to allow the off gas to accumulate. After 5 minutes of storing the asphalt mix in a vessel, a Drager "Multiwarn" electronic H₂S meter, equipped with a 20L/min pump, was connected to measure the accumulated H₂S concentration in the head space of the vessel. The results are shown in Table 2 below.

Table 2

	Urea (g)	1-[3-trimethoxysilyl propyl]urea (g)	Temperature, (°C)	H ₂ S (ppm)
Comparative Example 8	0	0	140	20
Comparative Example 9	0	0	150	28
Comparative Example 10	0	0	160	54
Example 11	0	1.54	150	22
Example 12	1.54	0	150	3
Example 13	0.77	0	150	2
Example 14	0.15 4	0	150	26
Example 15	0.77	0	160	2
Example 16	0.77	0	150	2

Discussion

Heating sulphur-bitumen mixtures leads to the evolution of H₂S. With increasing mixing temperatures,

the concentration of H_2S emitted increases (as can be seen from Comparative Examples 1,4,6). It was found that adding urea or a urea derivative resulted in lower amounts of H_2S being detected. The effect of urea on reducing the H_2S concentration is also operational at higher mixing temperatures (as can be seen from Comparative 6 and Example 7).

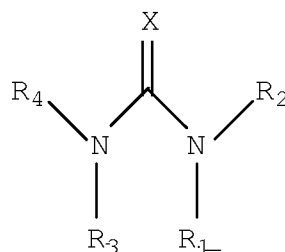
On heating sulphur asphalt mixes, H_2S is evolved. The concentration of H_2S increases with increasing asphalt mixing temperature (as can be seen from Comparative Examples 8-10). Addition of urea or a urea derivative leads to a pronounced reduction in the level of H_2S detected, (as can be seen from Comparative Example 9 and Examples 11 and 12). By varying the dosage level of urea (Examples 12-14) it was found that H_2S concentrations as low as 2 ppm were detected when using 0.77g urea (equivalent to 0.05 %, by weight of the asphalt mixture).

C L A I M S

1. Bituminous composition comprising from 20 wt% to 99.9 wt% of bitumen and from 0.01 wt% to 10 wt% of an aminic compound selected from carbamides, thiocarbamides, carbamates and thiocarbamates, and mixtures thereof.

2. Composition according to Claim 1 additionally comprising from 0.5 to 75 wt% of sulphur, by weight of the bituminous composition.

3. Composition according to claim 1 or 2, wherein the carbamides and thiocarbamides are selected from compounds of formula I:



(I)

wherein X is O or S and wherein R¹ to R⁴ are each individually selected from hydrogen and ci-cis hydrocarbyl groups optionally substituted with one or more functional groups.

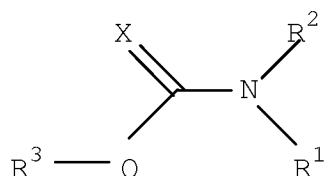
4. Composition according to Claim 3 wherein X is O.

5. Composition according to Claim 3 or 4 wherein the C1-C18 hydrocarbyl groups are selected from ci-cis aliphatic hydrocarbyl groups, C₃-C₁₈ alicyclic groups, and C₃-C₁₈ aromatic groups.

6. Composition according to any of Claims 3 to 5 wherein the functional groups are selected from amino, alkoxy, amine ethoxylates, olefinic, alcohol ethoxylates, carbonyl, carboxy esters, amides, silyl ethers, thiols and thio ethers.

7. Composition according to Claim 3 or 4 wherein R^1 to R^4 is hydrogen.

8. Composition according to Claim 1 or 2 wherein the carbamates and thiocarbamates are selected from compounds of formula (II) :



(II)

wherein X is O or S and wherein R^1 to R^3 are each individually selected from hydrogen and ci-cis hydrocarbyl groups optionally substituted with one or more functional groups .

9. Composition according to Claim 8 wherein X is O .

10. Composition according to Claim 8 or 9 wherein the C_1 - C_{18} hydrocarbyl groups are selected from ci-cis aliphatic hydrocarbyl groups, C_3 - C_{18} alicyclic groups, and C_3 - C_{18} aromatic groups.

11. Composition according to any of Claims 8 to 10 wherein the functional groups are selected from amino, alkoxy, amine ethoxylates, olefinic, alcohol ethoxylates, carbonyl, carboxy esters, amides, silyl ethers, thiols and thio ethers.

12. Composition according to Claim 8 or 9 wherein R^1 to R^3 is hydrogen.

13. Asphalt composition comprising the bitumen composition as claimed in any one of claims 1 to 12 and filler and/or aggregate.

14. Process for manufacturing a bituminous composition according to any of Claims 1 to 12, the process comprising the steps of:

(i) heating bitumen;

(ii) optionally mixing the hot bitumen so obtained with sulphur in an amount in the range of from 0.5 wt% to 75 wt%;

wherein from 0.01 wt% to 10 wt% of an aminic compound is added in at least one of the steps (i) or (ii), all weight % being by weight of the bituminous composition.

15. Process for manufacturing the asphalt composition according to Claim 13, the process comprising the steps of:

(i) heating bitumen;

(ii) heating aggregate;

(iii) mixing the hot bitumen with the hot aggregate in a mixing unit to form an asphalt composition;

optionally wherein from 0.5 wt% to 75 wt% of sulphur, is added in at least one of steps (i), (ii) or (iii);

and wherein from 0.01 wt% to 10 wt% of aminic compound, is added in at least one of the steps (i), (ii) or (iii), all weight% being by weight of bituminous composition comprising bitumen, aminic compound and optionally sulphur .

16. Use of an aminic compound selected from carbamides, thiocarbamides , carbamates, thiocarbamates , and mixtures thereof, for reducing % S emissions from a bituminous composition wherein the bituminous composition comprises from 20 wt% to 99.9 wt% of bitumen and from 0.01 wt% to 10 wt% of an aminic compound selected from carbamides, thiocarbamides, carbamates and thiocarbamates, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/061100

A. CLASSIFICATION OF SUBJECT MATTER		
INV. C08L95/00	C08K5/205	C08K5/21 C08K5/39 C08K5/405
ADD.		
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 C08K CIOL		
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		
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X	wo 2005/059016 AI (SHELL INT RESEARCH [NL] ; SHELL CANADA LTD [CA] ; DEME IMANTS [CA]) 30 June 2005 (2005-06-30)	1-16
Y	page 5, lines 19-22 ; claims 1-11 page 5, line 32 - page 6, line 3 the whole document	1-16
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☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "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 "P" document published prior to the international filing date but later than the priority date claimed "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 when the document is taken alone "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		
Date of the actual completion of the international search		Date of mailing of the international search report
1 September 2011		12/09/2011
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer ol de Scheper, Bernd

INTERNATIONAL SEARCH REPORT

International application No

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