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Fortsættes ...

DESCRIPTIONTECHNICAL FIELD

5 The present invention belongs to the field of bituminous compositions and their performance additives. More specifically, it relates to bituminous compositions comprising phosphoric derivatives and to their process of preparation.

 The invention also relates to the use of these bituminous compositions in the fields of road applications, in particular in the manufacture of road binders, such as hot bituminous
10 mixes, cold bituminous mixes, asphalts and surface coatings, and in the fields of industrial applications, for example in the manufacture of internal and external coatings.

PRIOR ART

15 The use of bitumen in the manufacture of materials for road and industrial applications has been known for a long time: bitumen is the main hydrocarbon binder used in the field of road construction or civil engineering. In order to be able to be used as binder in these different applications, the bitumen has to exhibit certain mechanical and dynamic properties.

 In general, conventional bitumens do not simultaneously exhibit all of the required
20 qualities. Bituminous compositions are used in the preparation of binders for various surface coatings and in particular as road surface coatings, provided that these compositions exhibit, in combination, a certain number of mechanical and/or dynamic characteristics. The mechanical properties of bituminous compositions are determined by standardized tests of the different mechanical characteristics, such as the softening point, the penetrability and the
25 rheological characteristics in predetermined tension.

 Numerous studies have related to the improvement in the mechanical, elastic and/or rheological properties of bituminous compositions.

 It has been known for a long time that the addition of various polymers to these conventional bitumens makes it possible to favorably modify the mechanical properties of the
30 latter and to form bitumen/polymer compositions having mechanical qualities which are improved with respect to those of the bitumens alone.

 In addition, it is known that the stability of the bitumen/polymer compositions can be improved by chemical coupling of the polymer to the bitumen. This chemical coupling, conventionally carried out by crosslinking of the polymer, makes it possible in addition to
35 broaden the range of use of the bitumen/polymer compositions. Mention may be made of the documents FR 2 376 188, FR 2 429 241, FR 2 528 439 and EP 0 360 656 as examples of a process involving a random or block copolymer of styrene and of a conjugated diene crosslinked with sulfur. The document FR 2 528 439 relates in particular to crosslinking with a polysulfide. The document EP 0 360 656 describes the use of a sulfur-donating vulcanization

accelerator used alone or in combination with chemically non-bonded sulfur and/or a polysulfide or a non-sulfur-donating vulcanization accelerator.

The bitumen/crosslinked polymer compositions thus obtained are known under the acronym "PmB", for Polymer-modified Bitumen, or "PmA", for Polymer-modified Asphalt. For reasons of clarity, we will use only the acronym PmB for the bitumen/crosslinked polymer compositions. The crosslinking of the bitumen/polymer compositions confers on them very good properties in terms of stability on storage, cohesiveness, elongational capability and resistance to aging.

Phosphoric acid and/or polyphosphoric acid has been used since the 1970s to improve the rheological properties of bitumens or bituminous compositions, in particular for increasing their consistency. Mention may be made, by way of example, of the document US 3 751 278, which describes a manufacturing process employing phosphoric acid for increasing the viscosity at high temperature without decreasing the consistency at ambient temperature.

Some acidic adjuvants have also been used to obtain bitumen/polymer compositions having a reinforced multigrade nature. In patent application EP 703 949, the authors have in addition demonstrated that the mechanical and/or rheological properties could be improved; in particular, the plasticity interval could be widened by using specific acidic inorganic adjuvants. The authors cite in particular phosphoric acids, sulfonic acids, sulfuric acids and their mixtures.

In the document WO9714753, the authors have shown that it is possible to widen the plasticity interval of the bitumen/sulfur-crosslinked polymer compositions by incorporating, in said compositions, an inorganic adjuvant of the acid or acid anhydride type after the phase of crosslinking with sulfur.

Another problem related to the use of bituminous compositions concerns the release of hydrogen sulfide, denoted H_2S , during their process of preparation or their use. The emission of H_2S is greater for the bitumen/crosslinked polymer compositions as a result of the use of sulfur-donating crosslinking agent in their process of preparation. Hydrogen sulfide (H_2S) is a colorless and toxic gas exhibiting a characteristic odor at a very low concentration. For reasons of safety and of environmental constraints, the reduction, indeed even the suppression, of hydrogen sulfide emissions during the production of bituminous compositions, in particular of bitumen/crosslinked polymer compositions, constitutes an industrial challenge.

Solutions have been provided in the literature for reducing hydrogen sulfide emissions during the manufacture or the use of bituminous compositions. In particular, the addition of an agent capable of trapping hydrogen sulfide (H_2S) during the crosslinking of bituminous compositions has been provided in order to overcome this disadvantage. Mention may be made, by way of example, of the organic or inorganic metal salts described in the international application WO2005065177 as capable of trapping H_2S . The process employed for reducing the releases of H_2S consists in introducing, into a reactor containing a premixed bitumen/polymer composition, an organic or inorganic metal salt. The metal salt, added in bulk to the reactor, is subsequently stirred in the reactor during the crosslinking reaction.

US 2006/081152 discloses asphalt compositions that can be prepared in free air and which meet the SUPERPAVE™ specifications. These compositions comprise in particular an additive for reducing gaseous emissions and an acid compound.

5 US 4,056,218 discloses a soldering flux that can be used for soldering copper, stainless steel and copper-plated stainless steel. The soldering flux is in the form of a viscous fluid or an emulsion and comprises phosphoric acid, a copper-based material and an organic material chosen from polyethers and/or polyimines.

FR 2 254 609 discloses the addition of compounds to a bitumen in order to reduce emissions of hydrogen sulfide, and in particular the use of copper carbonate.

10 The applicant company has been interested in the effectiveness of the agents capable of neutralizing and/or trapping H₂S in the processes for the preparation of bituminous compositions, in particular bitumen/crosslinked polymer compositions employing acidic inorganic adjuvants.

15 The object of the present invention is the improvement in the mechanical and dynamic properties, in particular the plasticity interval, of bituminous compositions, while reducing the risks of H₂S emissions during the preparation and/or the use of such bituminous compositions.

20 Another object of the invention is to obtain bituminous compositions which release low amounts of H₂S, preferably amounts of less than 10 ppm, more preferably of less than or equal to 1 ppm, during the preparation and/or the use (transportation, loading, unloading and storage) of such bituminous compositions, it being understood that the temperatures for preparation and/or use are conventionally between 90°C and 200°C and that the content of H₂S is measured according to a conventional method for assaying H₂S in the liquid phase.

The present invention also relates to a process for the preparation of such bituminous compositions.

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BRIEF DESCRIPTION

30 In the context of the preparation of bituminous compositions, the applicant company has discovered that, surprisingly, the use of an acidic adjuvant has a negative effect on the effectiveness of certain agents capable of neutralizing and/or trapping hydrogen sulfide (H₂S).

In particular, the applicant company has demonstrated that the acidic adjuvant deactivates said agents capable of neutralizing and/or trapping hydrogen sulfide (H₂S).

35 The applicant company has additionally discovered that the selection of certain specific agents capable of neutralizing and/or trapping hydrogen sulfide (H₂S) makes it possible to overcome this disadvantage. The specific combination of an acidic adjuvant and of an agent capable of neutralizing and/or trapping hydrogen sulfide (H₂S) makes it possible to obtain a bituminous composition having reduced H₂S emissions while improving the mechanical and/or dynamic properties of said composition. The use of such a combination is particularly advantageous for bitumen/crosslinked polymer compositions.

The applicant company has also discovered that, in order to obtain this combined effect, the agent capable of neutralizing and/or trapping hydrogen sulfide (H_2S) and the acidic adjuvant can be used together or successively, the order of introduction having no effect.

For reasons of simplicity, the term " H_2S scavenger" will be used systematically in the
5 continuation of the present patent application to refer to an agent capable of neutralizing and/or trapping hydrogen sulfide (H_2S).

Bituminous composition is understood to mean any bitumen composition comprising, in addition to the bitumen, at least one other constituent, for example an elastomer, and/or at least one additive.

10 According to the invention, the aim of the invention is achieved by a composition of performance additives for bitumen or bituminous compositions comprising an acidic adjuvant chosen from phosphoric acids, polyphosphoric acids and their mixtures and a H_2S scavenger chosen from organic or inorganic copper salts.

According to the invention, the H_2S scavenger is advantageously chosen from copper
15 hydroxycarbonates and mixtures thereof with copper oxides, hydroxides, hydrates, carbonates, carboxylates, nitrates and phosphates.

According to the invention, the aim of the invention is also achieved by the use of a H_2S scavenger in order to reduce the H_2S emissions of bitumen or of a bituminous composition treated with an acidic adjuvant, said H_2S scavenger and said acidic adjuvant
20 being as described above.

According to a specific embodiment, the use of a H_2S scavenger to reduce the H_2S emissions of bitumen or of a bituminous composition treated with an acidic adjuvant is such that the acidic adjuvant and the H_2S scavenger are in the form of a package of additives as described above.

25 According to the invention, the aim of the invention is also achieved by a process for the preparation of a bituminous composition, in which bitumen, an acidic adjuvant and a H_2S scavenger are brought into contact, the operation being carried out at temperatures of between $90^\circ C$ and $200^\circ C$, preferably between $120^\circ C$ and $200^\circ C$ and more preferably between $170^\circ C$ and $190^\circ C$ and with stirring for a period of time of at least 10 minutes, advantageously
30 of at least 2 hours, preferably between 20 minutes and 6 hours, more preferably between 30 minutes and 2 hours, said H_2S scavenger and said acidic adjuvant being as defined above.

According to a specific embodiment, the proportion of acidic adjuvant is between 0.05% and 15% by weight, preferably between 0.05% and 5% by weight and more preferably between 0.05% and 2% by weight, the percentages by weight being calculated with respect to
35 the total weight of the bituminous composition.

According to another specific embodiment, the proportion of H_2S scavenger is between 0.05% and 5% by weight, preferably between 0.1% and 3% by weight and more preferably between 0.1% and 1% by weight, the percentages by weight being calculated with respect to the total weight of the bituminous composition.

According to an alternative form, the process comprises the heating of the bitumen at a temperature of between 90°C and 200°C, preferably between 120°C and 200°C and more preferably between 170°C and 190°C, for at least 10 minutes, preferably between 20 minutes and 6 hours and more preferably between 30 minutes and 2 hours, with stirring, followed by the addition of the acidic adjuvant and of the H₂S scavenger, the reaction medium subsequently being maintained at temperature for at least 10 minutes with stirring, preferably between 20 minutes and 6 hours and more preferably between 30 minutes and 2 hours.

Advantageously, the process additionally comprises a stage of addition of 0.5% to 10% by weight, preferably between 1% and 6% by weight and more preferably between 1.5% and 4% by weight of an elastomer, it being understood that the bituminous composition is then a bitumen/polymer composition and that the percentages by weight are calculated with respect to the total weight of the bitumen/polymer composition.

According to a preferred specific embodiment, the elastomer is chosen from sulfur-crosslinkable elastomers and the process additionally comprises a stage of crosslinking of said elastomer by a sulfur-donating coupling agent added in an amount capable of providing from 0.1% to 20% by weight, advantageously from 1% to 10% by weight, preferably from 1% to 6% by weight and more preferably from 2% to 5% by weight of free sulfur with respect to the weight of sulfur-crosslinkable elastomer in said composition, it being understood that the bituminous composition is then a bitumen/crosslinked polymer composition.

The sulfur-donating coupling agent is advantageously chosen from the group consisting of elemental sulfur, hydrocarbyl polysulfides, sulfur-donating vulcanization accelerators and the mixtures of such products with one another and/or with non-sulfur-donating vulcanization accelerators.

According to a preferred alternative form, the elastomer is chosen from random or block copolymers of a monovinylaromatic hydrocarbon and of a conjugated diene.

The elastomer advantageously comprises between 5% and 50% by weight, preferably between 15% and 40% by weight, of monovinylaromatic hydrocarbon.

The elastomer is preferably chosen from random or block copolymers of styrene and of a conjugated diene.

According to a specific development, the weight-average molecular weight of the elastomer is between 10 000 and 600 000 daltons, preferably between 30 000 and 400 000 daltons.

According to the invention, the aim of the invention is also achieved by a bituminous composition capable of being obtained by the preparation process as defined above.

The invention also relates to a bituminous binder comprising a bituminous composition as defined above.

The invention also relates to an asphalt comprising a bituminous binder as described above and inorganic and/or synthetic fillers.

In addition, the invention relates to a bituminous mix comprising a bituminous binder as described above, aggregates and optionally inorganic and/or synthetic fillers.

DETAILED DESCRIPTION

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Other advantages and characteristics will emerge more clearly from the description which will follow, the specific embodiments of the invention of which are given as nonlimiting examples.

10 According to a specific embodiment, a package of performance additives comprises an acidic adjuvant and a H₂S scavenger.

Package of additives is understood to mean a composition comprising at least two additives. The package of additives can comprise additives alone or dispersed/dissolved in an inert solvent, in particular of mineral oil type, according to processes well known in the field of additives for bitumen. In the field of additivation, the term "package" is commonly used to
15 identify a composition of additives. The term "concentrate of additives" can also be employed to denote the package of additives, in particular when the latter is provided in the form of a solution.

Performance additives for bitumen or bituminous composition is understood to mean additives which are capable of being incorporated in a bituminous composition, for example in
20 relation to their compatibility, their solubility or their stability in said bitumen or said bituminous composition, and which confer on it improved properties, in comparison with the non-additivated bitumen or bituminous composition. These properties can be mechanical and/or dynamic and/or can relate to environmental and safety problems, for example problems of H₂S emissions.

25 The acidic adjuvant is preferably chosen from phosphoric acids, polyphosphoric acids and their mixtures.

Various grades of phosphoric acid and/or of polyphosphoric acid comprising different amounts of orthophosphoric acid are commercially available. Commercial phosphoric acids generally comprise from 50% to 200% of orthophosphoric acid.

30 The term "polyphosphoric acid" refers to concentrated grades of phosphoric acid (H₃PO₄) of greater than 95%, generally between 97% and 118%, where the percentage corresponds to the apparent concentration of H₃PO₄. Polyphosphoric acid is represented by the formula H_{n+2}P_nO_{3n+1} in which $n \geq 2$. Polyphosphoric acid is generally a mixture of pyrophosphoric acid (n=2), triphosphoric acid (n=3) and higher acids (n>3). Phosphoric and
35 polyphosphoric acids can comprise other acids, such as sulfuric acid and/or hydrofluoric acid, as impurities, at concentrations conventionally ranging up to 2%.

The H₂S scavenger is chosen from organic or inorganic copper salts.

According to the invention, the H₂S scavenger is chosen from copper hydroxycarbonates and mixtures thereof with copper oxides, hydroxides, hydrates,

carbonates, carboxylates, nitrates and phosphates.

The ratio by weight of the H₂S scavenger with respect to the acidic adjuvant can advantageously be between 1:300 and 100:1, preferably between 1:10 and 10:1 and more preferably between 1:10 and 5:1.

5 The package of performance additives can be composed solely of the H₂S scavenger and of the acidic adjuvant, alone or as a mixture in one or more inert solvents, it being understood that said H₂S scavenger and said acidic adjuvant can respectively comprise up to 2% by weight of impurities without, for all that, it being considered that they are not used alone. The solvent has to be inert with respect to the acidic adjuvant and/or the H₂S
10 scavenger.

Generally, the amount of solvent in the package of additives is between 1% and 95%, preferably between 10% and 90%, more preferably between 20% and 80% and more preferably still between 40% and 60% by weight, the percentages by weight being calculated with respect to the total weight of said package of additives.

15 The inert solvent or solvents will preferably be chosen so as to dissolve both the H₂S scavenger and the acidic adjuvant. For example, the solvent will be chosen from mineral oils.

Preferably, the package of additives is composed solely of the H₂S scavenger and of the acidic adjuvant, the ratio by weight of the H₂S scavenger with respect to the acidic adjuvant being as described above. Such a package of additives is stable on storage and can
20 be added directly during the preparation of the bitumen/crosslinked polymer composition.

The package of additives can be used directly in the treatment of the bitumen or bituminous compositions. In particular, the package of additives can advantageously be used in the process for the preparation of bituminous compositions, preferably of bitumen/polymer compositions and more preferably of bitumen/crosslinked polymer compositions employing a
25 sulfur-donating coupling agent.

According to an alternative form, the H₂S scavenger and the acidic adjuvant as described above can be used separately in the treatment of the bitumen or bituminous compositions, in particular in the preparation of bitumen/polymer compositions and preferably of bitumen/crosslinked polymer compositions employing a sulfur-donating coupling agent.

30 According to a specific embodiment, a process for the preparation of a bitumen/crosslinked polymer composition comprises a stage of treatment with the acidic adjuvant and the H₂S scavenger described above at a temperature of between 90°C and 200°C, preferably between 120°C and 200°C and more preferably between 170°C and 190°C, for a period of time of at least 10 minutes, preferably of between 20 minutes and 6 hours and
35 more preferably of between 30 minutes and 2 hours.

According to a specific embodiment, the process for the preparation of a bitumen/crosslinked polymer composition comprises, for example, the following stages:

- a bitumen and a sulfur-crosslinkable elastomer are introduced into a reactor,

- the mixture is stirred until a homogeneous bitumen/elastomer mixture is obtained and is heated at a temperature of between 90°C and 200°C, preferably between 120°C and 200°C and more preferably between 170°C and 190°C, for a period of time of at least 10 minutes, preferably of between 20 minutes and 6 hours and more preferably of between 1 hour and 5 hours,

- said elastomer is crosslinked by addition of a sulfur-donating coupling agent to the reaction medium in an amount suitable for providing from 0.1% to 20% by weight, advantageously from 1% to 10% by weight, preferably from 1% to 6% by weight and more preferably from 2% to 5% by weight of free sulfur, with respect to the total weight of the elastomer, while keeping the reaction medium stirred at a temperature of between 90°C and 200°C, preferably between 120°C and 200°C and more preferably between 170°C and 190°C, for a period of time of at least 10 minutes, preferably of between 20 minutes and 6 hours and more preferably of between 30 minutes and 2 hours,

- the H₂S scavenger described above is added, the reaction medium being maintained at a temperature of between 90°C and 200°C, preferably between 120°C and 200°C and more preferably between 170°C and 190°C, for a period of time of at least 10 minutes, preferably of between 20 minutes and 6 hours and more preferably of between 30 minutes and 2 hours,

- the acidic adjuvant described above is added, the reaction medium being maintained at a temperature of between 90°C and 200°C, preferably between 120°C and 200°C and more preferably between 170°C and 190°C, for a period of time of at least 10 minutes, preferably of between 20 minutes and 6 hours and more preferably of between 30 minutes and 2 hours.

According to another specific embodiment, the process for the preparation of a bitumen/crosslinked polymer composition comprises, for example, the following stages:

- a bitumen and a sulfur-crosslinkable elastomer are introduced into a reactor,

- the mixture is stirred until a homogeneous bitumen/elastomer mixture is obtained and is heated at a temperature of between 90°C and 200°C, preferably between 120°C and 200°C and more preferably between 170°C and 190°C, for a period of time of at least 10 minutes, preferably of between 20 minutes and 6 hours and more preferably of between 1 hour and 5 hours,

- said elastomer is crosslinked by addition of a sulfur-donating coupling agent to the reaction medium in an amount suitable for providing from 0.1% to 20% by weight, advantageously from 1% to 10% by weight, preferably from 1% to 6% by weight and more preferably from 2% to 5% by weight of free sulfur, with respect to the total weight of the elastomer, while keeping the reaction medium stirred at a temperature of between 90°C and 200°C, preferably between 120°C and 200°C and more preferably between 170°C and 190°C, for a period of time of at least 10 minutes, preferably of between 20 minutes and 6 hours and more preferably of between 30 minutes and 2 hours,

- the acidic adjuvant and the H₂S scavenger described above are added simultaneously, the reaction medium being maintained at a temperature of between 90°C and

200°C, preferably between 120°C and 200°C and more preferably between 170°C and 190°C, for a period of time of at least 10 minutes, preferably of between 20 minutes and 6 hours and more preferably of between 30 minutes and 2 hours.

5 The simultaneous addition of the H₂S scavenger and of the acidic adjuvant has the advantage of reducing the duration of preparation of the bitumen/crosslinked polymer composition and of improving the plasticity interval of said composition. Use may advantageously be made of the package of additives as described above in the stage of simultaneous addition of the acidic adjuvant and of the H₂S scavenger.

For each stage, the temperatures may or may not be identical.

10 The bitumen according to the present invention can comprise one or more bitumen bases. The bitumen bases can result from different sources. Mention may first of all be made of bitumen bases of natural origin, those present in natural bitumen or natural asphalt deposits or bituminous sands.

15 The bitumen bases can advantageously originate from the refining of crude oil, preferably from the atmospheric and/or vacuum distillation of oil. The bitumen bases can optionally be blown, visbroken and/or deasphalted.

The bitumen bases can be chosen from bitumens of hard grade or of soft grade.

The different bitumen bases obtained by the refining processes can be combined with one another in order to obtain the best technical compromise.

20 The bitumen bases used can also be chosen from bitumens fluxed by addition of volatile solvents, of fluxes of petroleum origin and/or of fluxes of plant origin.

The bitumen is advantageously chosen from road bitumens of grades 10/20 to 160/220 and special bitumens of all grades.

25 The bitumen represents between 90% and 99.3% by weight, preferably between 94% and 99% by weight, of the bitumen/crosslinked polymer composition.

The amount of acidic adjuvant added represents advantageously between 0.05% and 15% by weight, preferably between 0.05% and 5% by weight and more preferably between 0.05% and 2% by weight of the total weight of the bitumen/crosslinked polymer composition.

30 The amount of H₂S scavenger added represents advantageously between 0.05% and 5% by weight, preferably between 0.1% and 3% by weight and more preferably between 0.1% and 1% by weight of the total weight of the bitumen/crosslinked polymer composition.

35 In the specific embodiment described above, the acidic adjuvant can be incorporated in the bitumen/crosslinked polymer mixture before or after the H₂S scavenger, it also being possible for a simultaneous incorporation to be envisaged, in particular by addition of a package of additives as described above to the bitumen/crosslinked polymer mixture.

The amount of elastomer introduced into the reactor represents advantageously between 0.5% and 10% by weight, preferably between 1% and 6% by weight and more preferably between 1.5% and 4% by weight of the total weight of the bitumen/crosslinked polymer composition.

The weight-average molecular weight of the elastomer is advantageously between 10 000 and 600 000 daltons, preferably between 30 000 and 400 000 daltons.

5 The elastomer is preferably chosen from random or block copolymers of a monovinylaromatic hydrocarbon and of a conjugated diene. In particular, the elastomer advantageously comprises between 5% and 50% by weight, preferably between 15% and 40% by weight, of monovinylaromatic hydrocarbon.

10 The elastomer is advantageously chosen from random or block copolymers of styrene and of a conjugated diene, such as butadiene, isoprene, chloroprene, carboxylated butadiene or carboxylated isoprene. Random or block copolymers of styrene and butadiene will preferably be chosen.

The elastomer can consist of one or more copolymers chosen from block copolymers, with or without a random hinge, of styrene and butadiene, of styrene and isoprene, of styrene and chloroprene, of styrene and carboxylated butadiene or of styrene and carboxylated isoprene.

15 Preferably, the copolymer of styrene and of conjugated diene is chosen from di- or triblock copolymers of styrene and butadiene, of styrene and isoprene, of styrene and carboxylated butadiene or of styrene and carboxylated isoprene which have styrene contents and weight-average molecular weights lying within the ranges defined above.

20 According to an alternative form, the elastomer is chosen from random or block copolymers of styrene and butadiene including from 50% to 95% and more particularly from 60% to 95% by weight of units resulting from butadiene. In addition, the proportion of units having a 1,2- double bond resulting from the butadiene can advantageously be between 12% and 50% by weight of said copolymer. The elastomer can, for example, be a styrene/butadiene copolymer of high vinyl type, that is to say having a content of 1,2- double bonds resulting from the butadiene of greater than 20% by weight of said copolymer.

25 The sulfur-donating coupling agents which can be used are of very varied nature and are chosen as a function of the elastomer to be crosslinked in the bitumen/crosslinked polymer composition.

30 The sulfur-donating coupling agent is advantageously chosen from the group consisting of elemental sulfur, hydrocarbyl polysulfides, sulfur-donating vulcanization accelerators and the mixtures of such products with one another and/or with non-sulfur-donating vulcanization accelerators.

35 The elemental sulfur capable of being used to constitute, in part or in all, the crosslinking agent is advantageously flowers of sulfur and preferably crystalline sulfur in the orthorhombic form known under the name of alpha-sulfur.

The vulcanization accelerators are either hydrocarbyl polysulfides or sulfur-donating vulcanization accelerators or non-sulfur-donating vulcanization accelerators. The hydrocarbyl polysulfides can be chosen from those which are defined in the patent FR 2 528 439 cited as example and/or incorporated by reference in the present patent application. The sulfur-

donating vulcanization accelerators can be chosen from thiuram polysulfides, such as, for example, tetrabutylthiuram disulfides, tetraethylthiuram disulfides and tetramethylthiuram disulfides. The non-sulfur-donating vulcanization accelerators which can be used can be sulfur-comprising compounds chosen in particular from mercaptobenzothiazole and its derivatives, dithiocarbamates and its derivatives and monosulfides of thiuram and its derivatives.

Mention may be made, for example, of zinc 2-mercaptobenzothiazole, zinc dibutyldithiocarbamate or tetramethylthiuram monosulfide. For further details with regard to the sulfur-donating and non-sulfur-donating vulcanization accelerators which can be used according to the invention, reference may be made to the patents EP 0 360 656, EP 0 409 683 and FR 2 528 439 cited as example and/or incorporated by reference in the present patent application.

Adhesion agents and/or surface-active agents can also be added to the bitumen/crosslinked polymer composition according to any known process. They are generally chosen from alkylamine derivatives, alkylpolyamine derivatives, alkylamidopolyamine derivatives, alkylamidopolyamine derivatives and derivatives of quaternary ammonium salts, taken alone or as a mixture. The amount of adhesion agents and/or surface-active agents in the bitumen/crosslinked polymer composition is, for example, between 0.2% and 2% by weight, preferably between 0.5% and 1% by weight, with respect to the total weight of the bitumen/crosslinked polymer composition.

The order of introduction of the different constituents does not appear to influence the mechanical and/or dynamic properties of the bitumen/crosslinked polymer composition thus obtained. Nevertheless, it will be preferable to add the elastomer before or at the same time as the sulfur-donating coupling agent for better homogeneity of the composition.

According to an alternative form, the elastomer and the sulfur-donating coupling agent can be introduced simultaneously in the form of a mother solution, according to any known process, during the process for the preparation of the bitumen/crosslinked polymer composition. The mother solution generally comprises a hydrocarbon oil acting as thinning agent, from 5% to 40% by weight of elastomer and from 0.02% to 15% by weight of coupling agent, preferably from 10% to 35% by weight of elastomer and from 0.1% to 5% by weight of coupling agent.

The bitumen/crosslinked polymer compositions can be used as is or else diluted, according to any known process, with variable proportions of bitumen or of a composition according to the invention having different characteristics, in order to form bitumen/polymer binders having a chosen content of crosslinked elastomer which can either be equal to (undiluted composition) or else less (diluted composition) than the content of crosslinked elastomer of the corresponding initial bitumen/polymer compositions.

Generally, the diluting of the bitumen/crosslinked polymer compositions can be carried out either directly subsequent to the obtaining of said compositions, when a virtually

immediate use of the resulting bitumen/polymer binders is required, or else after a more or less prolonged duration of storage of the bitumen/crosslinked polymer compositions, when a delayed use of the resulting bitumen/polymer binders is envisaged. The bitumen for the diluting of a bitumen/crosslinked polymer composition according to the invention can be
5 chosen from the bitumens described above. If appropriate, the bitumen used for the diluting may have been itself pretreated with an acidic adjuvant and/or a H₂S scavenger according to the invention.

The bitumen/crosslinked polymer compositions obtained by the preparation process described above have improved mechanical and dynamic properties, in particular a reinforced
10 multigrade nature. Reinforced multigrade nature is understood to mean the fact that these bitumen/crosslinked polymer compositions exhibit a broad plasticity interval. Said interval is defined as the difference between the ring-and-ball softening temperature, which reveals the properties under hot conditions of the binder or bitumen/polymer composition, and the Fraass
15 breaking point, which reveals the properties under cold conditions of the bitumen/crosslinked polymer composition. The bituminous binder consisting of/or based on the bitumen/crosslinked polymer composition will show better resistance to the stresses under hot conditions and under cold conditions as the plasticity interval widens.

More generally, the bituminous compositions obtained by the preparation process according to the present invention exhibit improved mechanical and dynamic properties, in
20 particular a better consistency, with a lower needle penetrability at 25°C and/or a higher ring-and-ball temperature.

In addition, at the temperatures of preparation and/or of use (transportation, loading, unloading and storage) conventionally of between 90°C and 200°C, the H₂S emissions originating from the bituminous compositions, in particular from the bitumen/crosslinked
25 polymer compositions according to the invention, are greatly reduced. The content of H₂S emitted is in particular less than 10 ppm, more preferably less than or equal to 1 ppm, the content of H₂S being measured according to a conventional method for the assaying of H₂S in the liquid phase.

Various uses of the bituminous compositions obtained according to the invention are
30 envisaged. In particular, the bituminous compositions, in particular the bitumen/polymer compositions and the bitumen/crosslinked polymer compositions, according to the invention can be used in the preparation of bituminous binders.

According to a specific embodiment, a bituminous binder comprises a bituminous composition as described above.

35 The bituminous binder according to the invention can in its turn be employed to prepare a combination with aggregates, in particular road aggregates.

As regards the road applications, the invention is targeted in particular at bituminous mixes as materials for the construction and the maintenance of road foundations and their surfacing, and also in carrying out all road works.

Bituminous mix is understood to mean a mixture of a bituminous binder with aggregates and optionally inorganic and/or synthetic fillers.

The bituminous mix comprises a bituminous binder as described above and optionally inorganic and/or synthetic fillers, preferably chosen from fines, sand, stone chips and recycled milled products. The aggregates are inorganic and/or synthetic aggregates, in particular recycled milled products, with dimensions of greater than 2 mm, preferably of between 2 mm and 20 mm.

The bituminous binder described above can advantageously be used to prepare a surface coating, a hot bituminous mix, a cold bituminous mix, a cold-poured bituminous mix or a grave emulsion.

As regards the road applications, the invention is also targeted at asphalts as materials for constructing and covering sidewalks.

Asphalt is understood to mean a mixture of bituminous binder with inorganic and/or synthetic fillers.

An asphalt comprises a bituminous binder as described above and mineral fillers, such as fines, sand or stone chips, and/or synthetic fillers. The mineral fillers are composed of fines (particles with dimensions of less than 0.063 mm), of sand (particles with dimensions of between 0.063 mm and 2 mm) and optionally of stone chips (particles with dimensions of greater than 2 mm, preferably of between 2 mm and 4 mm).

The asphalts exhibit 100% compactness and are mainly used to construct and cover sidewalks, whereas the mixes have a compactness of less than 100% and are used to construct roads. Unlike the mixes, the asphalts are not compacted with a roller when being put in place.

Another aspect of the invention is the use of a bituminous composition, preferably a bitumen/crosslinked polymer composition, in various industrial applications, in particular for preparing a leaktight coating, a membrane or a seal coat.

As regards the industrial applications of the bituminous compositions, mention may be made of the preparation of leaktight membranes, of noise-reduction membranes, of insulating membranes, of surface coatings, of carpet tiles or of seal coats.

EXAMPLES

The invention is illustrated by the following examples, given without implied limitation.

In these examples, the amounts and percentages are expressed by weight, unless otherwise indicated.

For the record, throughout the present patent application, the following properties of the bitumens are measured as shown in table 1 below:

Table 1

Property	Abbreviation	Unit	Measurement
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			standard
Needle penetrability at 25°C	P25	1/10 mm	EN 1426
Ring-and-ball softening temperature	RBT	°C	EN 1427
Fraass breaking point	Fraass	°C	EN 12593

Bitumen

The bitumen used results from vacuum residues from the direct distillation of crude oil.

- 5 The bitumen has a P25 of 43 1/10 mm.

Elastomer

- 10 Styrene/butadiene/styrene block copolymer, comprising 30.5% by weight of styrene and comprising 69.5% by weight of butadiene. The content of 1,2-vinyl groups is 27.8% by weight, with respect to the total weight of copolymer. The copolymer has a weight-average molecular weight (Mw) of 142 500 daltons and a polydispersity index I_p of 1.09.

Acidic adjuvant

15

115% Polyphosphoric acid, denoted **PPA**; CAS No. 8017-16-1.

Sulfur-donating coupling agent

20

Flowers of sulfur; CAS No. 7704-34-9.

Scavenger

- 25 2: The characteristics of the different scavengers S_x tested are listed in the following table

Table 2

Reference of the scavenger S_x	Product	Trade name/Supplier	CAS No.
S_1	Zinc carboxylate	Nalco	
S_2	Copper(II) hydroxy carbonate	Merck	12069-69-1
S_3	Magnesium hydroxy carbonate	VWR International	12125-28-9
S_4	Calcium carbonate	Sigma-Aldrich	471-34-1

S ₅	Zinc oxide	VWR International	1314-13-2
S ₆	Calcium oxide	Aldrich	1305-78-8
S ₇	Magnesium oxide	VWR International	1309-48-4
S ₈	Copper(II) oxide	VWR International	1317-38-0

Bitumen/crosslinked polymer compositions C₁ to C₈

5 The bitumen/crosslinked polymer compositions C₁ to C₈ are prepared according to a preparation process employing the following three stages:

First stage: preparation of the bitumen/crosslinked polymer compositions without PPA: C^o₁ to C^o₉

10 The following are introduced into the reactor:

97.71% by weight of the bitumen,
2.22% by weight of the elastomer.

The mixture is stirred at high intensity, that is to say at a high shear rate, in order to obtain a mixture which is homogeneous at the micron scale, and is heated at 185°C for approximately 4 hours.

0.07% by weight of the sulfur-donating coupling agent is subsequently added.

The mixture is stirred at low intensity and is heated at 185°C for 2 hours.

The percentages of each of the constituents are calculated with respect to the weight of the bitumen/crosslinked polymer composition resulting from the first stage.

Second stage: treatment of the H₂S emissions in order to obtain bitumen/crosslinked polymer compositions without PPA but with scavenger: C^s₁ to C^s₉

25 The second stage consists in adding 0.2% by weight of the scavenger S_x. The scavenger S_x is introduced into the reactor and then the mixture is stirred while maintaining the temperature at 185°C for 20 minutes. The percentage of scavenger S_x is calculated with respect to the weight of the bitumen/crosslinked polymer composition resulting from the second stage.

30 For the compositions C^s₁ to C^s₈, the scavenger S_x was added directly to the reactor, without predissolution.

For the composition C^s₉, the scavenger S₂ was added as a 20% by weight solution in a mineral oil.

Third stage: acid treatment with PPA in order to obtain bitumen/crosslinked polymer compositions with PPA and scavenger: C₁ to C₈

35

The third stage consists in adding 0.8% by weight of PPA to the reaction medium. The PPA is introduced into the reactor and then the mixture is stirred while maintaining the temperature at 185°C for 30 minutes. The percentage of PPA is calculated with respect to the weight of the bitumen/crosslinked polymer composition resulting from the third stage.

The amounts used are as follows: 967.3 g of bitumen, 22 g of the elastomer, 0.7 g of sulfur, 2 g of scavenger S_x and 8 g of PPA.

Measurement of the H_2S emissions

The measurement of the H_2S emissions is carried out according to a conventional method for assaying H_2S . The measurement of the H_2S emissions consists in sparging gaseous nitrogen into the bitumen/crosslinked polymer composition to be tested, maintained at 185°C, followed by the measurement of the content of H_2S trapped in the gaseous nitrogen by means of a H_2S gas detector. The calculation of the concentration of H_2S in the liquid phase is based on the initial weight of the bitumen/crosslinked polymer composition tested.

This measurement does not have the purpose of being representative of the content of H_2S present in the gaseous headspace in real time but has the aim of comparing the effectiveness of the scavengers used under identical conditions, by determining the presence or the absence of a release of H_2S . Thus, we have set a limiting threshold for release of H_2S above which we consider that the effectiveness of the scavenger is insufficient. This method makes it possible, in addition, to demonstrate the phenomenon of deactivation of certain scavengers in the presence of an acidic adjuvant.

The measurement of the H_2S emissions is carried out after each of the three stages described above. The results are listed in table 3 below.

Table 3

PmB (reference)		PmB + S_x (reference)		PmB + S_x + PPA	
C°_x	H_2S (ppm)	C^{S_x}	H_2S (ppm)	C_x	H_2S (ppm)
C°_1	>100	C^{S_1}	<1*	C_1^B	>100
C°_2	>100	C^{S_2}	<1*	C_2^A	<1*
C°_3	>100	C^{S_3}	>100	C_3^B	>100
C°_4	>100	C^{S_4}	>100	C_4^B	>100
C°_5	>100	C^{S_5}	>100	C_5^B	>100
C°_6	>100	C^{S_6}	>100	C_6^B	>100
C°_7	>100	C^{S_7}	>100	C_7^B	>100
C°_8	>100	C^{S_8}	<1*	C_8^B	<1*

C°_9	>100	C^{s_9}	<1*	C_9^B	<1*
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*detection limit of the H₂S gas detector

^A according to the invention

^B outside the invention

5 In the light of the results gathered together in table 3, the following comments may be made:

- During the first stage of the process for the preparation of the bitumen/polymer composition C°_x , the crosslinking with sulfur of the elastomer is accompanied by a release of H₂S. The contents of H₂S measured exceed the limiting threshold of 100 ppm.

10 - During the treatment of the second stage, the scavengers S₁ to S₈ can be differentiated according to their effectiveness in trapping and/or neutralizing the H₂S. For the bitumen/crosslinked polymer composition C^{s_3} , C^{s_4} , C^{s_5} , C^{s_6} or C^{s_7} , the addition, respectively, of 0.2% by weight of the scavenger S₃, S₄, S₅, S₆ or S₇ is not sufficient to reduce the release of H₂S to a content of less than 100 ppm. The scavengers S₃, S₄, S₅, S₆ and S₇ consequently prove to be scavengers which are relatively ineffective in reducing H₂S emissions in
15 bitumen/crosslinked polymer compositions.

- On the other hand, the scavengers S₁, S₂ and S₈ are particularly effective. Success is achieved in reducing the H₂S emissions of the bitumen/crosslinked polymer compositions C^{s_1} , C^{s_2} and C^{s_8} down to a content below the detection limit of the H₂S gas detector (1 ppm).

20 Furthermore, it is noticed that the addition of the scavenger S₂ in solution in a mineral oil does not damage the effectiveness of said scavenger in reducing the H₂S emissions of the bitumen/crosslinked polymer composition C^{s_9} .

- During the acid treatment of the third stage, the measured content of H₂S in the bitumen/crosslinked polymer composition C₁ is, surprisingly, markedly greater than the limiting threshold of 100 ppm, whereas the measurement carried out after the second stage on the
25 bitumen/crosslinked polymer composition C^{s_1} had revealed virtually no presence of H₂S (<1 ppm). This increase in the content of H₂S before and after the third stage (20 min after the introduction of the PPA) reflects a phenomenon of release of H₂S responsible for the deactivation of the scavenger S₁.

30 In addition, this phenomenon of release of H₂S is also observed for the bitumen/crosslinked polymer compositions C^{s_3} , C^{s_5} and C^{s_6} respectively comprising the scavengers S₃, S₅ and S₆. This is because a significant increase in the content of H₂S ($\Delta H_2S \geq 100$ ppm) is observed before and after the third stage (30 min after the introduction of the PPA).

35 Thus, the results demonstrate that the addition of PPA deactivates the scavengers S₁, S₃, S₅ and S₆ and produces a phenomenon of release of H₂S in the bitumen/crosslinked polymer compositions C₁, C₃, C₅ and C₆.

For the bitumen/crosslinked polymer compositions C^{s_4} and C^{s_7} respectively comprising the scavengers S₄ and S₇, it is not possible to go by these measurements in ruling on the

presence of a phenomenon of deactivation of the scavenger by the PPA insofar as the scavengers S_4 and S_7 are not effective enough as H_2S scavenger.

- The effectiveness of the scavengers S_2 and S_8 is particularly noteworthy in the presence of PPA since success is achieved in suppressing virtually all of the H_2S emissions in the bitumen/crosslinked polymer compositions C_2 and C_8 .

In addition, the presence of PPA does not damage the effectiveness of the scavengers S_2 and S_8 as a phenomenon of release of H_2S in the bitumen/crosslinked polymer compositions C_2 and C_8 is not observed. The scavengers S_2 and S_8 are thus compatible with an acid treatment of bitumen/crosslinked polymer composition, in particular a treatment with PPA.

Furthermore, the effectiveness of the scavenger S_2 is maintained after treatment with PPA when said scavenger is added in solution in a mineral oil (bitumen/crosslinked polymer composition C_9).

In conclusion, the inorganic or organic copper salts are particularly effective in comparison with the other inorganic or organic metal salts as H_2S scavenger of bitumen/crosslinked polymer compositions employing an acid treatment, in particular a treatment with PPA.

Properties of the bitumen/crosslinked polymer compositions

The characteristics of the different bitumen/crosslinked polymer compositions, measured according to the abovementioned standards, are recorded in the following table 4:

Table 4

Bitumen/crosslinked polymer composition	$C_{s_1}^R$	C_1^B	C_2^A	C_8^B
H_2S scavenger	S_1	S_1	S_2	S_8
PPA presence yes/no	no	yes	yes	yes
P25 (1/10mm)	34	31	27	28
RBT ($^{\circ}C$)	62	65.4	68.4	66.8
Fraass ($^{\circ}C$)	-8	-12	-10	-9
Plasticity interval (ΔRBT -Fraass)	70	77.4	78.4	75.8

^A according to the invention

^B outside the invention

^R reference

The comparison of the RBT and Fraass results of the bitumen/crosslinked polymer compositions C_{s_1} and C_1 confirms the increase in the plasticity interval due to the acid treatment with PPA described in the prior art.

The use of the scavengers S_2 and S_8 according to the present invention does not affect the effect of the acid treatment on the mechanical and dynamic properties of the bitumen/crosslinked polymer composition, in particular on the plasticity interval. On the contrary, the bitumen/crosslinked polymer composition C_2 has a plasticity interval widened in comparison with that of the bitumen/crosslinked polymer composition C_1 . With regard to the plasticity interval of the composition C_8 , it remains comparable to that of the composition C_1 .

Use of a package of H_2S scavenger/acidic adjuvant additives: effect on the H_2S emissions and on the properties of the bitumen/crosslinked polymer compositions

- Preparation of the packages of additives P_2 and P_8 :

Two packages of additives P_2 (according to the invention) and P_8 (outside the invention) are prepared by mixing 20% by weight of scavenger S_2 (package P_2) or S_8 (package P_8) and 80% by weight of PPA. The scavengers S_2 and S_8 are soluble in the PPA and the packages of additives P_2 and P_8 are provided in the form of a homogeneous solution.

- Preparation of the bitumen/crosslinked polymer compositions C'_2 and C'_8 :

Bitumen/crosslinked polymer compositions C'_2 (according to the invention) and C'_8 (outside the invention) were prepared by respectively adding the package of additives P_2 (composition C'_2) or P_8 (composition C'_8) to the bitumen/crosslinked polymer composition C°_2 or C°_8 obtained on conclusion of the first stage as described above.

- Measurement of the H_2S emissions:

The measurement of the H_2S emissions is carried out after the preparation of the bitumen/crosslinked polymer composition (first stage) and after the addition of the package of additives. The results are listed in table 5 below.

Table 5

PmB (reference)		PmB + Package of additives	
C°_x	H_2S (ppm)	C_x	H_2S (ppm)
C°_2	>100	C'_2^A	<1*
C°_8	>100	C'_8^B	<1*

^A according to the invention

^B outside the invention

In the light of the preceding results, it is noticed that the addition of the package of additives P_2 or P_8 on conclusion of the first stage of the process for the preparation of the

bitumen/crosslinked polymer composition C_2° or C_8° does not damage the effectiveness of the scavenger in trapping the H_2S emissions. This is because a phenomenon of release of H_2S in the bitumen/crosslinked polymer compositions C_2' and C_8' is not observed. The scavengers S_2 and S_8 and the PPA can thus be introduced all at once in the form of a package of additives, which makes it possible to shorten the duration of preparation of a bitumen/crosslinked polymer composition while reducing the H_2S emissions.

- Properties of the bitumen/crosslinked polymer compositions:

The characteristics of the different bitumen/crosslinked polymer compositions, measured according to the abovementioned standards, are listed in the following table 6:

Table 6

Bitumen/crosslinked polymer composition	C_1^B	C_2^A	C_8^B	$C_2'^A$	$C_8'^B$
H_2S scavenger	S_1	S_2	S_8	S_2	S_8
PPA presence yes/no	yes	yes	yes	yes	yes
P25 (1/10mm)	31	27	28	23	22
RBT ($^{\circ}C$)	65.4	68.4	66.8	71	70.4
Fraass ($^{\circ}C$)	-12	-10	-9	-10	-10
Plasticity interval (ΔRBT -Fraass)	77.4	78.4	75.8	81	80.4

^A according to the invention

^B outside the invention

The addition of the package of additives P_2 or P_8 does not affect the effect of the acid treatment on the mechanical and dynamic properties of the bitumen/crosslinked polymer composition, in particular on the plasticity interval. On the contrary, the bitumen/crosslinked polymer compositions C_2' and C_8' have a plasticity interval widened in comparison with that of the bitumen/crosslinked polymer composition C_1 .

In conclusion, the process for the preparation of the bitumen/crosslinked polymer compositions according to the invention makes it possible to substantially reduce the releases of hydrogen sulfide (H_2S) in the presence of an acidic adjuvant, while having mechanical and dynamic properties comparable to those of the bitumen/crosslinked polymer compositions of the prior art.

Patentkrav

- 1.** Sammensætning af funktionelle additiver til bitumen eller bituminøse sammensætninger bestående udelukkende af et surt tilsætningsstof valgt fra
- 5 phosphorsyrer, polyphosphorsyrer og deres blandinger og af en H₂S-scavenger valgt fra kobber-hydroxyl-karbonater og deres blandinger med oxider, hydroxider, hydrater, karbonater, carboxylater, nitrater og kobber-phosphater, hvor nævnte sure tilsætningsstof og nævnte H₂S-scavenger er alene eller i en blanding i et eller flere solventer der er inerte i forhold til det sure tilsætningsstof og H₂S-
- 10 scavengeren, hvor det forstås, at nævnte H₂S-scavenger og nævnte sure tilsætningsstof kan henholdsvis omfatte op til 2 vægtprocent af urenheder.
- 2.** Anvendelse af en H₂S-scavenger til at reducere H₂S-emissionerne fra bitumen eller af en bituminøs sammensætning behandlet med et surt tilsætningsstof valgt
- 15 fra phosphorsyrer, polyphosphorsyrer og deres blandinger, hvor nævnte H₂S-scavenger er valgt fra kobber-hydroxyl-karbonater og deres blandinger med oxider, hydroxider, hydrater, karbonater, carboxylater, nitrater og kobber-phosphater.
- 20 **3.** Fremgangsmåde til fremstillingen af en bitumen eller af en bituminøs sammensætning, hvilken fremgangsmåde omfatter behandlingen af en bitumen eller af en bituminøs sammensætning med en H₂S-scavenger valgt fra kobber-hydroxyl-karbonater og deres blandinger med oxider, hydroxider, hydrater, karbonater, carboxylater, nitrater og kobber-phosphater og med et surt
- 25 tilsætningsstof valgt fra phosphorsyrer, polyphosphorsyrer og deres blandinger, hvor H₂S-scavengeren og det sure tilsætningsstof anvendes separat.
- 4.** Fremgangsmåde til fremstillingen af en bitumen eller af en bituminøs sammensætning, hvilken fremgangsmåde omfatter behandlingen af en bitumen
- 30 eller af en bituminøs sammensætning med en H₂S-scavenger valgt fra kobber-hydroxyl-karbonater og deres blandinger med oxider, hydroxider, hydrater, karbonater, carboxylater, nitrater og kobber-phosphater og med et surt tilsætningsstof valgt fra phosphorsyrer, polyphosphorsyrer og deres blandinger, hvilken fremgangsmåde omfatter den direkte tilsætning til bitumenen eller til den

bituminøse sammensætning af en sammensætning af tilsætningsstoffer omfattende H₂S-scavengeren og det sure tilsætningsstof.

5 **5.** Fremgangsmåde ifølge et hvilket som helst af kravene 3 og 4, til fremstillingen af en bitumen-/polymer-sammensætning.

6. Fremgangsmåde ifølge krav 5, til fremstillingen af en bitumen-/tværbunden polymersammensætning ved anvendelse af et svovldonerende koblingsmiddel.

10 **7.** Fremgangsmåde til fremstillingen af en bituminøs sammensætning ifølge et hvilket som helst af kravene 3 til 6, **kendetegnet ved, at** bitumen, det sure tilsætningsstof og H₂S-scavengeren bringes i kontakt, hvilket udføres ved temperaturer på mellem 90 °C og 200 °C og med omrøring for en tidsperiode på mindst 10 minutter.

15

8. Fremgangsmåde ifølge et hvilket som helst af kravene 3 til 7, **kendetegnet ved, at** andelen af surt tilsætningsstof er mellem 0,05 og 15 vægtprocent, hvor vægtprocenterne beregnes i forhold til den totale vægt af den bituminøse sammensætning.

20

9. Fremgangsmåde ifølge et hvilket som helst af kravene 3 til 8, **kendetegnet ved, at** andelen af H₂S-scavenger er mellem 0,05 og 5 vægtprocent, hvor vægtprocenterne beregnes i forhold til den totale vægt af den bituminøse sammensætning.

25

10. Fremgangsmåde ifølge et hvilket som helst af kravene 6 til 9, **kendetegnet ved, at** den omfatter opvarmningen af bitumenen ved en temperatur på mellem 90 °C og 200 °C i mindst 10 minutter med omrøring, efterfulgt af tilsætningen af det sure tilsætningsstof og af H₂S-scavengeren, hvor reaktionsmediet efterfølgende opretholdes ved temperatur i mindst 10 minutter med omrøring, og **ved, at** nævnte fremgangsmåde endvidere omfatter et trin til tilsætning af 0,5 til 10 vægtprocent af en elastomer, hvor det forstås, at den bituminøse sammensætning derefter er en bitumen-/polymer-sammensætning og hvor

vægtprocenterne beregnes i forhold til den totale vægt af bitumenen/polymer sammensætning.

- 11.** Fremgangsmåde ifølge krav 10, **kendetegnet ved, at** elastomeren vælges
5 fra svovl-tværbindelige elastomerer og **ved, at** fremgangsmåden endvidere
omfatter et trin til tværbinding af nævnte elastomer med et svovldonerende
koblingsmiddel tilsat i en mængde i stand til at tilvejebringe fra 0,1 til 20
vægtprocent af fri svovl i forhold til vægten af svovl-tværbindelig elastomer i
nævnte sammensætning, hvor det forstås, at den bituminøse sammensætning
10 derefter er en bitumen-/tværbunden polymersammensætning.
- 12.** Fremgangsmåde ifølge et hvilket som helst af kravene 7 til 11, **kendetegnet
ved, at** det svovldonerende koblingsmiddel vælges fra gruppen bestående af
elementær svovl, hydrocarbyl-polysulfider, svovldonerende
15 vulkaniseringsacceleratorer og blandingerne af sådanne produkter med hinanden
og/eller med ikke-svovldonerende vulkaniseringsacceleratorer.
- 13.** Fremgangsmåde ifølge et hvilket som helst af kravene 11 til 12,
kendetegnet ved, at elastomeren er valgt fra tilfældige eller blok-copolymerer af
20 et monovinylaromatisk carbonhydrid og af en konjugeret dien.
- 14.** Bituminøs sammensætning i stand til at blive opnået ved en fremgangsmåde
til fremstilling som defineret i et hvilket som helst af kravene 3 til 13.
- 25 **15.** Asfalt, **kendetegnet ved, at** det omfatter en bituminøs sammensætning
ifølge krav 14 og mineralske og/eller syntetiske fyldstoffer.
- 16.** Bituminøs blanding, **kendetegnet ved, at** den omfatter en bituminøs
sammensætning ifølge krav 14 og granulater og eventuelt mineralske og/eller
30 syntetiske fyldstoffer.