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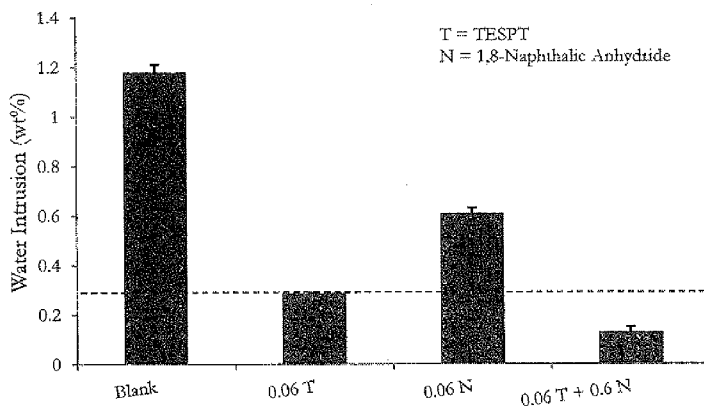
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(54) **Title:** SULPHUR CEMENT PRE-COMPOSITION AND PROCESS FOR PREPARING SUCH SULPHUR CEMENT PRE-COMPOSITION

Figure 1



(57) **Abstract:** The invention provides a sulphur cement pre-composition comprising sulphur and an unsaturated anhydride coupling agent, and wherein the unsaturated anhydride coupling agent is present in an amount in the range of 0.05-10 wt%, based on the total weight of the sulphur cement pre-composition.

WO 2014/009501 A1

SULPHUR CEMENT PRE-COMPOSITION AND PROCESS FOR PREPARING
SUCH SULPHUR CEMENT PRE-COMPOSITION

Field of the Invention

The present invention provides a sulphur cement pre-composition and a process for the preparation of a sulphur cement pre-composition. The invention further provides a process for the preparation of a sulphur cement product, a sulphur cement product and the use of such sulphur cement pre-composition or sulphur cement product in sulphur cement, sulphur mortar, sulphur concrete or sulphur-extended asphalt.

Background of the Invention

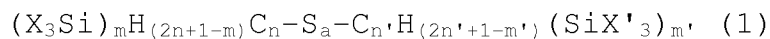
Sulphur cement generally refers to a product comprising at least sulphur and a filler. To improve the properties of the sulphur cement, the sulphur may be modified using a sulphur modifier. Such modifiers are known in the art. Usual sulphur cement fillers are particulate inorganic materials.

Sulphur cement-aggregate composites generally refer to a composite comprising both sulphur cement and aggregate. Examples of sulphur cement-aggregate composites are sulphur mortar, sulphur concrete and sulphur-extended asphalt. Sulphur-extended asphalt is asphalt, i.e. typically aggregate with a binder that contains filler and a residual hydrocarbon fraction, wherein part of the binder has been replaced by sulphur, usually modified sulphur.

It is known to use organosilane compounds as a stabilising agent in sulphur cement or sulphur cement-aggregate compositions to improve water durability. In US 4,164,428 for example, a modified sulphur composition

(often referred to a plasticized sulphur composition) comprising at least 50% by weight of sulphur, a sulphur modifier (often referred to a sulphur plasticizer), a finely divided particulate mineral suspending agent, and an organosilane stabilising agent is disclosed. It is mentioned that suitable organosilanes have the general molecular formula $R-Si(OR')_3$, wherein R' is a low molecular weight alkyl group and R is an organic radical having at least one functional group, usually bonded to the silicon atom by a short alkyl chain. Gamma-mercaptopropyltrimethoxysilane is mentioned as a preferred organosilane.

In US 2010/0242807 A1, the preparation of a sulphur cement pre-composition has been described which sulphur cement pre-composition comprises sulphur and a polysulphide-containing organosilane, which organosilane has the general molecular formula:



wherein a is an integer in the range of from 2 to 8, X and X' each are, independently, a hydrolysable group, n and n' each are, independently, an integer in the range of from 1 to 4, and m and m' each are, independently, an integer in the range of from 1 to $(2n+1)$. The sulphur cement pre-composition is prepared by admixing sulphur with the polysulphide-containing organosilane in an amount of at least 0.3 wt% based on the weight of the total composition. In general terms it has been mentioned that the sulphur cement pre-composition may also comprise a sulphur modifier.

Although the sulphur cement products obtained in accordance with US 4,164,428 and US 2010/0242807 A1 already display attractive properties in terms of durability, there is, however, still room in improving

the properties of the sulphur cement product in terms of water uptake and to improve the process for preparing the sulphur cement pre-composition in terms of the release of volatile organic compounds.

5 Summary of the Invention

It has now been found that this can be established when use is made of a particular sulphur cement pre-composition.

10 Accordingly, the present invention relates to a sulphur cement pre-composition comprising sulphur and an unsaturated anhydride coupling agent, and wherein the unsaturated anhydride coupling agent is present in an amount in the range of 0.05-10 wt%, based on the total weight of the sulphur cement pre-composition.

15 The sulphur cement pre-composition is especially effective when it is mixed with a particulate inorganic material which comprises alkali and/or alkaline earth metal ions on the surface of the particulate inorganic material. The use of the sulphur cement pre-composition
20 in accordance with the present invention in the manufacture of sulphur cement products provides sulphur cement products that attractively display less water uptake, whereas at the same time during the manufacturing of the sulphur cement product release of volatile organic
25 compounds is avoided.

The invention in a further aspect provides a process for the preparation of a sulphur cement pre-composition, comprising admixing sulphur with an unsaturated anhydride coupling agent, and wherein the unsaturated anhydride
30 coupling agent is present in an amount in the range of 0.05-10 wt%, based on the total weight of the sulphur cement pre-composition.

The invention in a further aspect provides a sulphur cement product comprising sulphur, an unsaturated anhydride coupling agent, and a particulate inorganic material which comprises alkali and/or alkaline earth metal ions on the surface of the particulate inorganic material, and wherein the unsaturated anhydride coupling agent is present in an amount in the range of 0.05-10 wt%, based on the total weight of the sulphur cement product.

The invention in still a further aspect provides a process for the preparation of a sulphur cement product comprising the steps of:

- (a) admixing sulphur with an unsaturated anhydride coupling agent, and with a particulate inorganic material which comprises alkali and/or alkaline earth metal ions on the surface of the particulate inorganic material at a temperature at which sulphur is molten to obtain a molten sulphur cement product, and wherein the unsaturated anhydride is present in an amount in the range of 0.05-10 wt%, based on the total weight of the sulphur cement product; and
- (b) solidifying the molten sulphur cement product.

The invention in another aspect provides the use of the sulphur cement pre-composition according to the invention or the sulphur cement product according to the present invention in sulphur cement, sulphur mortar, sulphur concrete or sulphur-extended asphalt.

In the context of the present invention an unsaturated anhydride is defined as an anhydride which comprises an unsaturated hydrocarbon 'backbone' adjacent to a cyclic anhydride functional group, i.e. the 5- or 6-membered ring of the cyclic anhydride contains a carbon-carbon double bond.

Detailed Description of the Invention

In accordance with the present invention the sulphur pre-composition comprises sulphur and an unsaturated anhydride.

5 The unsaturated anhydride is suitably selected from the group consisting of maleic anhydride, phthalic anhydride, naphthalic anhydride, preferably 1,8-naphthalic anhydride, and/or a derivative thereof. Suitably, also any mixture of these unsaturated
10 anhydrides can be used.

 Preferably, the unsaturated anhydride is 1,8-naphthalic anhydride and/or a derivative thereof.

 The unsaturated anhydride coupling agent is present in an amount in the range of from 0.05-10 wt%, based on
15 the total weight of the sulphur cement pre-composition. Preferably, the unsaturated anhydride coupling agent is present in an amount in the range of from 0.1-10 wt%, more preferably 0.1-5 wt%, based on the total weight of the sulphur cement pre-composition.

20 The sulphur to be used in accordance with the present invention is preferably elemental sulphur.

 The sulphur cement product of the present invention comprises sulphur, an unsaturated anhydride coupling agent, and a particulate inorganic material which
25 comprises alkali and/or alkaline earth metal ions on the surface of the particulate inorganic material, and wherein the unsaturated anhydride coupling agent is present in an amount in the range of 0.05-10 wt%, based on the total weight of the sulphur cement product.
30 Preferably, the unsaturated anhydride coupling agent is present in an amount in the range of from 0.1-10 wt%, more preferably 0.1-5 wt%, based on the total weight of the sulphur cement product.

The particulate inorganic material to be used in accordance with the present invention preferably comprises a carbonate-based material. Suitably, the carbonate-based material is present in an amount in the range of from 5 to 100 wt%, based on the total weight of the particulate inorganic material. Preferably, the carbonate-based material is present in an amount in the range of from 20 to 100 wt%, based on the total weight of particulate inorganic material. Most preferably, the carbonate-based material is present in an amount in the range of from 40 to 100wt%, based on the total weight of particulate inorganic material.

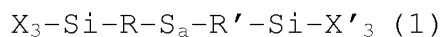
The carbonate-based material is preferably an alkali and/or alkaline earth metal carbonate.

The carbonate-based material is suitably calcium carbonate or dolomite.

Preferably, the carbonate-based material is calcium carbonate.

Suitably, the particulate inorganic material may further comprises a silica or silicate, and the product further comprises a polysulphide-containing organosilane which is present in an amount in the range of 0.05-10 wt%, based on the total weight of the sulphur cement product. Preferably, the polysulphide-containing organosilane is present in an amount in the range of from 0.1-10 wt%, more preferably 0.1-5 wt%, based on the total weight of the sulphur cement product.

Suitably, the polysulphide-containing organosilane has the general molecular formula



wherein a is 2 to 8, X and X' each are, independently, a hydrolysable group, R and R' each are, independently, an alkyl radical with 1 to 4 carbon atoms.

The use of such a polysulphide-containing organosilane in addition to the unsaturated anhydride has the advantage that the water uptake of the sulphur cement product to be prepared is considerably further decreased.

5 An advantage of the use of a polysulphide-containing organosilane with two functionalised organosilyl groups as compared to the known use of, for instance, gamma-mercaptopropyltrimethoxysilane as coupling agent in sulphur cement or sulphur cement-aggregate composites is
10 that the water uptake of the cement or cement-aggregate composite is further lowered.

Another advantage of the use of a polysulphide-containing organosilane with two functionalised organosilyl groups is that it also acts as a sulphur
15 modifier. Therefore, it is possible to prepare sulphur cement or a sulphur cement-aggregate composite with less sulphur modifier than usual whilst achieving the desired degree of sulphur modification or plastification.

Another advantage is that the sulphur cement
20 prepared according to the invention has improved mechanical properties as compared to sulphur cement prepared with other organosilanes, for example gamma-mercaptopropyltrimethoxysilane.

A further advantage of the use of a polysulphide-containing organosilane with two functionalised
25 organosilyl groups is that it has a far lower toxicity and a less unpleasant smell than gamma-mercaptopropyltrimethoxysilane.

In general molecular formula (1), a is an integer in
30 the range of from 2 to 8, preferably of from 2 to 6. X and X' each are, independently, a hydrolysable group, preferably a halogen, alkoxy, acyloxy or aryloxy group, more preferably a lower alkoxy group, for example methoxy

or ethoxy. R and R' each are, independently, an alkyl radical with 1 to 4 carbon atoms. R is preferably the same alkyl radical as R' and X is preferably the same hydrolysable group as X'. Particularly preferred
5 organosilanes are bis(3-triethoxysilylpropyl)tetrasulphide, bis(3-trimethoxysilylpropyl)disulphide, bis(3-trimethoxysilylpropyl)trisulphide, bis(3-trimethoxysilylpropyl)tetrasulphide.

10 The sulphur cement pre-composition comprising sulphur and the unsaturated anhydride can suitably be prepared by first admixing at least part of the sulphur and at least part of the unsaturated anhydride and subsequently admixing the remaining amounts of the
15 sulphur and the unsaturated anhydride.

The sulphur cement pre-composition comprising sulphur, the unsaturated anhydride and the polysulphide-containing organosilane can be prepared in a number of ways. Suitably, in the present process at least part of
20 the sulphur is first admixed with at least part of the unsaturated anhydride and at least part of the polysulphide-containing organosilane, and subsequently the remaining sulphur, unsaturated anhydride and polysulphide-containing organosilane is added to the
25 mixture so obtained in any possible order; at least part of the unsaturated anhydride is admixed with at least part of the polysulphide-containing organosilane and the mixture so obtained is admixed with the sulphur; at least part of the polysulphide-containing organosilane is
30 admixed with at least part of the sulphur and the mixture so obtained is admixed with the unsaturated anhydride; or at least part of the sulphur is admixed with at least part of the unsaturated anhydride and the mixture so

obtained is admixed with the polysulphide-containing organosilane.

Preferably, in the present process (a) at least part of the sulphur is admixed with at least part of the
5 unsaturated anhydride and at least part of the polysulphide-containing organosilane; (b) at least part of the sulphur is admixed with at least part of the polysulphide-containing organosilane and the mixture so
10 obtained is admixed with unsaturated anhydride; or (c) at least part of the polysulphide-containing organosilane is admixed with at least part of the unsaturated anhydride and the mixture so obtained is admixed with the sulphur.

More preferably, in the present process (a) at least part of the sulphur is admixed with at least part of the
15 unsaturated anhydride and at least part of the polysulphide-containing organosilane; or (b) at least part of the unsaturated anhydride is admixed with at least part of the polysulphide-containing organosilane and the mixture so obtained is admixed with the sulphur.

Most preferably, in the present process at least part of the sulphur is admixed with at least part of the
20 unsaturated anhydride and at least part of the polysulphide-containing organosilane. This means that most preferably at least part of the sulphur to be used is simultaneously admixed with at least part of the
25 unsaturated anhydride to be used and at least part of the polysulphide-containing organosilane to be used.

In a particularly attractive embodiment of the present invention in a first step the sulphur and the
30 unsaturated anhydride and at least part of the polysulphide-containing organosilane are admixed and in a second step the mixture so obtained is admixed with the

remaining part of the polysulphide-containing organosilane.

Suitably, in the present process sulphur modifier is present in amount in the range of from 0.05-10 wt%, preferably in an amount in the range of from 0.1-10 wt%, more preferably in an amount in the range of from 0.1-5 wt%, based on the total weight of the sulphur cement pre-composition.

Suitably, in the present process sulphur is present in an amount of at least 90 wt%, based on the total weight of the sulphur cement pre-composition.

When used at a cement plant, the present sulphur cement pre-composition may suitably be added in such amounts to an inorganic material that the need for stabilising agent is immediately satisfied. The sulphur cement product may be completed by adding additional sulphur. The sulphur cement pre-composition is typically solid under ambient conditions, in contrast to the generally liquid polysulphide-containing organosilane.

The sulphur cement pre-compositions according to the invention may be used in solid or molten state, for instance to prepare a sulphur cement product.

In accordance with the present invention, the unsaturated anhydride may first be dissolved in a small amount of solvent, for example an alcohol, in order to facilitate the admixing with the sulphur.

The polysulphide-containing organosilane may first be dissolved in a small amount of solvent, for example an alcohol or a hydrocarbon, in order to facilitate the admixing with the unsaturated anhydride and sulphur. The solvent preferably has a boiling point such it evaporates during the admixing step.

Preferably, in the process for the preparation of the sulphur cement pre-composition the unsaturated anhydride and sulphur are admixed at a temperature at which sulphur is molten. In another embodiment, the unsaturated anhydride, the polysulphide-containing organosilane and sulphur are admixed at a temperature at which sulphur is molten. Alternatively, the obtained sulphur cement pre-composition is heated and mixed at a temperature at which the sulphur is molten. The temperature at which sulphur is molten is typically above 118 °C, preferably in the range of from 120 to 150 °C, more preferably in the range of from 125 to 140 °C. Mixing at temperatures at which the sulphur is molten may provide a homogeneous distribution of the unsaturated anhydride and the polysulphide-containing organosilane in the sulphur. In case the sulphur, the unsaturated anhydride and the polysulphide-containing organosilane are admixed at a temperature at which sulphur is molten or the obtained sulphur cement pre-composition is heated and mixed at a temperature at which the sulphur is molten, the obtained sulphur cement pre-composition may be cooled to a temperature at which the sulphur solidifies. The solid sulphur cement pre-composition can be easily stored or transported.

As mentioned herein above the sulphur cement pre-composition can suitably be used to prepare a sulphur cement product. Reference herein to a sulphur cement product is to a sulphur cement, sulphur mortar, sulphur concrete or sulphur-extended asphalt.

A sulphur cement typically refers to a composition comprising sulphur or modified sulphur and a filler. Usual sulphur cement fillers are particulate inorganic materials with an average particle size in the range of

from 0.1 μm to 0.1 mm. The filler content of sulphur cement may vary widely, but is typically in the range of from 1 to 50 wt%, based on the total weight of the cement.

5 Sulphur cement-aggregate composites generally refer to a composite comprising both sulphur cement and a particulate inorganic material aggregate. Examples of sulphur cement-aggregate composites are sulphur mortar, sulphur concrete and sulphur-extended asphalt. Mortar
10 comprises fine aggregate, typically with particles having an average diameter between 0.1 and 5 mm, for example sand. Concrete comprises coarse aggregate, typically with particles having an average diameter between 5 and 40 mm. Sulphur-extended asphalt is asphalt, i.e. typically
15 aggregate with a binder that contains filler and a residual hydrocarbon fraction, wherein part of the binder has been replaced by sulphur, usually modified sulphur.

In the present process for preparation of sulphur cement product according to the invention, a sulphur
20 cement product is prepared by admixing in step (a) sulphur with a modifier which comprises the unsaturated anhydride, and with the particulate inorganic material which comprises alkali and/or alkaline earth metal ions on the surface of the particulate inorganic material at a
25 temperature at which sulphur is molten to obtain a molten sulphur cement product. In step (b), after the admixing step (a), the molten sulphur cement product is allowed to solidify. Typically, solidification takes place by allowing the molten sulphur cement product to cool down
30 to a temperature below the melt temperature of sulphur.

In step (a), a particulate inorganic material is admixed with sulphur and with a modifier. In case of a process for the preparation of sulphur cement, the

inorganic material is an inorganic filler. In the case
the process for preparing a sulphur cement product is
used for the preparation of a sulphur cement-aggregate
composite, the particulate inorganic material may be
5 filler and aggregate. The particulate inorganic material
that is admixed with the sulphur cement pre-composition
in step (a) may be any particulate inorganic material
known to be suitable as sulphur cement filler or
aggregate. Preferably, the particulate inorganic material
10 that is admixed in step (a) has oxide or hydroxyl groups
on its surface. Examples of suitable particulate
inorganic materials are silica, fly ash, limestone,
quartz, iron oxide, alumina, titania, carbon black,
gypsum, talc or mica, sand, gravel, rock or metal-
15 silicates.

In one embodiment of the invention, in step (a), a
particulate inorganic material is admixed with the
sulphur cement pre-composition. The conditions under
which the particulate inorganic material is admixed with
20 the sulphur cement pre-composition are preferably such
that the modifier comprised in the sulphur cement pre-
composition is allowed to react with the inorganic
material. The reaction time is typically in the range of
from 5 minutes to 3 hours, preferably of from 10 minutes
25 to 2 hours.

In another embodiment of the invention, in step (a)
a particulate inorganic material is admixed with an
unsaturated anhydride coupling agent, and is then
subsequently admixed with sulphur. In a preferred
30 embodiment of the invention, in step (a) a particulate
inorganic material is mixed with a polysulphide-
containing organosilane, is then subsequently mixed with

an unsaturated anhydride coupling agent, and is then subsequently admixed with sulphur.

The invention is further illustrated by means of the following non-limiting examples.

5 Examples

Experiment 1 (Comparative Examples 1-2 and Examples 1-2)
Preparation of Mortar Prisms

8 different 4 x 4 x 16 cm prisms of sulphur mortar were prepared (2 for each of the 4 experiments thus improving reliability), each weighing approximately 520 grams. Each prism contains 25 wt% sulphur previously dried at 60 °C, 60 wt% silicate-based sand (Euro Normsand) previously dried at 150 °C as fine aggregate, 15 wt% of Wigro® limestone filler (available from Ankerpoort) previously dried at 150 °C. The dosages of unsaturated anhydride modifier and/or TESPT (bis(triethoxysilylpropyl)tetrasulfide) modifier in comparative examples 1-2 and examples 1-2 are shown in Table 1 hereinbelow.

Table 1

	1,8-naphthalic anhydride (wt%)	TESPT (wt%)
Comparative Example 1	-	-
Comparative Example 2	-	0.06
Example 1	0.06	-
Example 2	0.06	0.06

20 All experiments were conducted in the following manner:

Appropriate quantities of sand and sulphur in each case were mixed at 140 °C until a homogeneous mixture was obtained. The appropriate quantity (if applicable) of

TESPT was added and the mix stirred for 5 minutes. The appropriate quantity of Wigro® filler was then added and the mixture stirred for a further 5 mins. The appropriate quantity (if applicable) of naphthalic anhydride was then added and the mix stirred for a further 10 minutes. The mixture was then poured into 4 x 4 x 16 cm silicone moulds which had been stored at 150 °C. Once cool, each thus-formed mortar prism was then demoulded.

Water Absorption

The mortar prisms of comparative examples 1-2 and examples 1-2 were immersed in water for 28 days. The mass increase was determined. The results and modifier concentrations used are shown in Figure 1. The mortars prepared with purely TESPT (comparative example 2) have a significantly lower water uptake than mortars prepared without modifier (comparative example 1). It is believed that this reflects an improved bonding between the silicate content of the filler/aggregate and sulphur.

The mortars prepared with purely 1,8-naphthalic anhydride (example 1) have a lower water uptake than those prepared without modifier. It is believed that this reflects an improved bonding between the carbonate content of the filler/aggregate and sulphur.

The mortars prepared with a combination of TESPT and 1,8-naphthalic anhydride (example 2) show an improved performance against those with purely TESPT (comparative example 2) and those with purely 1,8-naphthalic anhydride (example 1). It is believed that this demonstrates the complimentary selectivity of the TESPT and 1,8-naphthalic anhydride modifiers as the former improves the bonding between the silicate content of the filler/aggregate and the sulphur while the latter improves the bonding between

the carbonate content of the filler/aggregate and the sulphur.

Experiment 2 (Comparative Examples 3-4 and Examples 3-8)

Preparation of Mortar Prisms

5 16 different 4 x 4 x 16 cm prisms of sulphur mortar were prepared (2 for each example/comparative example thus improving reliability), each weighing approximately 520 grams. Each prism contains 25 wt% sulphur previously dried at 60 °C, 60 wt% calcium carbonate fine aggregate
10 (in this case Kalkzand which is available from de Hoop) previously dried at 150 °C, 15 wt% Wigro® limestone filler (available from Ankerpoort) previously dried at 150 °C. The dosages of 1,8-naphthalic anhydride modifier and/or TESPT modifier are shown in Table 2 as shown
15 hereinbelow.

Table 2

	1,8-naphthalic anhydride (wt%)	TESPT (wt%)
Comparative Example 3	-	-
Comparative Example 4	-	0.06
Example 3	0.06	-
Example 4	0.06	0.06
Example 5	0.06	0.12
Example 6	0.12	0.06
Example 7	0.12	0.12
Example 8	0.3	0.06

These comparative examples and examples were conducted in the following manner:

20 Appropriate quantities of sand, Wigro® filler and sulphur in each case were mixed at 140 °C until a homogeneous mixture was obtained. The appropriate

quantity (if applicable) of 1,8-naphthalic anhydride was added and the mix stirred for 10 minutes. The appropriate quantity (if applicable) of TESPT was then added and the mix stirred for a further 10 minutes. The mixture was then poured into 4 x 4 x 16 cm silicone moulds which had been stored at 150 °C. Once cool, each thus-formed mortar prism was then demoulded.

Water Absorption

The mortar prisms in comparative examples 3-4 and examples 3-8 were immersed in water for 2 months. The mass increase was determined. The results of experiments are shown in Figure 2. The experiment numbers and modifier concentrations are also shown.

The mortars prepared with purely TESPT (comparative example 4) have a lower water uptake than mortars prepared without modifier (comparative example 3). It is believed that this reflects a slight improvement in the bonding between the silicate content of the filler/aggregate and sulphur.

The mortars prepared with purely 1,8-naphthalic anhydride (example 3) have a significantly lower water uptake than those prepared without modifier or purely with TESPT (comparative examples 3 and 4 respectively). It is believed that this reflects an improved bonding between the carbonate content of the filler/aggregate and the sulphur.

The mortars prepared with a combination of TESPT and naphthalic anhydride (examples 4-8) show an improved performance against those with without modifier or purely with TESPT (comparative examples 3 and 4 respectively). However, those containing a combination of TESPT and 1,8-naphthalic anhydride show a slightly greater water

intrusion level than those with purely 1,8-naphthalic anhydride (example 3).

Experiment 3 (Comparative Examples 5-6 and Examples 9-14)

Preparation of Mortar Prisms

5 24 different 4 x 4 x 16 cm prisms of sulphur mortar were prepared (3 for each comparative example or example thus improving reliability), each weighing approximately 520 grams. Each prism contains 25 wt% sulphur previously dried at 60 °C, 60 wt% calcium carbonate fine aggregate
10 (in this case Kalkzand which is available from de Hoop) previously dried at 150 °C, 15 wt% of Wigro® limestone filler (available from Ankerpoort) previously dried at 150 °C. The dosages of the 1,8-naphthalic anhydride modifier and/or TESPT modifier are shown in Table 3
15 hereinbelow.

Table 3

Exp. No.	1,8-naphthalic anhydride (wt%)	TESPT (wt%)
Comparative Example 5	-	-
Comparative Example 6	-	0.06
Example 9	0.06	-
Example 10	0.06	0.06
Example 11	0.06	0.12
Example 12	0.12	0.06
Example 13	0.12	0.12
Example 14	0.3	0.06

All experiments were conducted in an analogous manner to those in Example 2.

Strength Retention

The flexural strength (measured by a 3-point bending test) of one mortar prism from each experiment was measured (henceforth labeled as 'dry strength').

5 The 2 remaining prisms from each experiment were then immersed in water for 2 months. The flexural strength of these mortar prisms was then measured ('wet strength'). Strength retention, defined as 'average wet strength'/'average dry strength' * 100 %, can be used as
10 a measure of the durability of a sample.

The 'dry strength' and strength retention for comparative examples 5-6 and examples 9-14 are shown in Figure 3. The experiment numbers and modifier concentrations are also shown.

15 The mortars prepared with purely TESPT (comparative example 6) have a similar strength retention to those prepared without modifier (comparative example 5).

 The mortars prepared with purely 1,8-naphthalic anhydride (example 9) show a much greater strength
20 retention than those prepared with TESPT (comparative example 6) or without modifier (comparative example 5).

C L A I M S

1. A sulphur cement pre-composition comprising sulphur and an unsaturated anhydride coupling agent, and wherein the unsaturated anhydride coupling agent is present in an amount in the range of 0.05-10 wt%, based on the total weight of the sulphur cement pre-composition.
2. A sulphur cement pre-composition according to claim 1, wherein the unsaturated anhydride is naphthalic anhydride and/or a derivative thereof.
3. A sulphur cement pre-composition according to claim 1 or 2 comprising in addition an polysulphide-containing organosilane coupling agent which is present in an amount in the range of 0.05-10 wt%, based on the total weight of the sulphur cement pre-composition.
4. A process for the preparation of a sulphur cement pre-composition, comprising admixing sulphur with an unsaturated anhydride coupling agent, and wherein the unsaturated anhydride coupling agent is present in an amount in the range of 0.05-10 wt%, based on the total weight of the sulphur cement pre-composition.
5. A process according to claim 4, wherein the unsaturated anhydride is naphthalic anhydride and/or a derivative thereof.
6. A process according to claim 4 or 5, wherein the sulphur is in addition mixed with an polysulphide-containing organosilane coupling agent which is present in an amount in the range of 0.05-10 wt%, based on the total weight of the sulphur cement pre-composition.
7. A sulphur cement product comprising sulphur, an unsaturated anhydride coupling agent, and a particulate inorganic material which comprises alkali and/or alkaline

earth metal ions on the surface of the particulate inorganic material, and wherein the unsaturated anhydride coupling agent is present in an amount in the range of 0.05-10 wt%, based on the total weight of the sulphur cement product.

5 8. A sulphur cement product according to claim 7, wherein the unsaturated anhydride is naphthalic anhydride and/or a derivative thereof.

9. A sulphur cement product according to claim 7 or 8,
10 wherein the particulate inorganic material comprises a carbonate-based material.

10. A sulphur cement product according to any one of claims 7-9, wherein the particulate inorganic material further comprises a silica or silicate, and the product
15 further comprises a polysulphide-containing organosilane coupling agent which is present in an amount in the range of 0.05-10 wt%, based on the total weight of the sulphur cement product.

11. A process for the preparation of a sulphur cement
20 product comprising the steps of:

(a) admixing sulphur with an unsaturated anhydride coupling agent, and with a particulate inorganic material which comprises alkali and/or alkaline earth metal ions on the surface of the particulate inorganic material at a
25 temperature at which sulphur is molten to obtain a molten sulphur cement product, and wherein the unsaturated anhydride is present in an amount in the range of 0.05-10 wt%, based on the total weight of the sulphur cement product; and

30 (b) solidifying the molten sulphur cement product.

12. A process according to claim 10, wherein the unsaturated anhydride is naphthalic anhydride and/or a derivative thereof.

13. A process according to claim 10 or 11, wherein the particulate inorganic material comprises a carbonate-based material.

5 14. A process according to claim 10 or 11, wherein the particulate inorganic material further comprises a silica or silicate, and the product further comprises a polysulphide-containing organosilane which is present in an amount in the range of 0.05-10 wt%, based on the total weight of the sulphur cement product.

10 15. The use of a sulphur cement pre-composition according to any one of claims 1-3 or the sulphur cement product according to any one of claims 7-10, in sulphur cement, sulphur mortar, sulphur concrete or sulphur-extended asphalt.

Figure 1

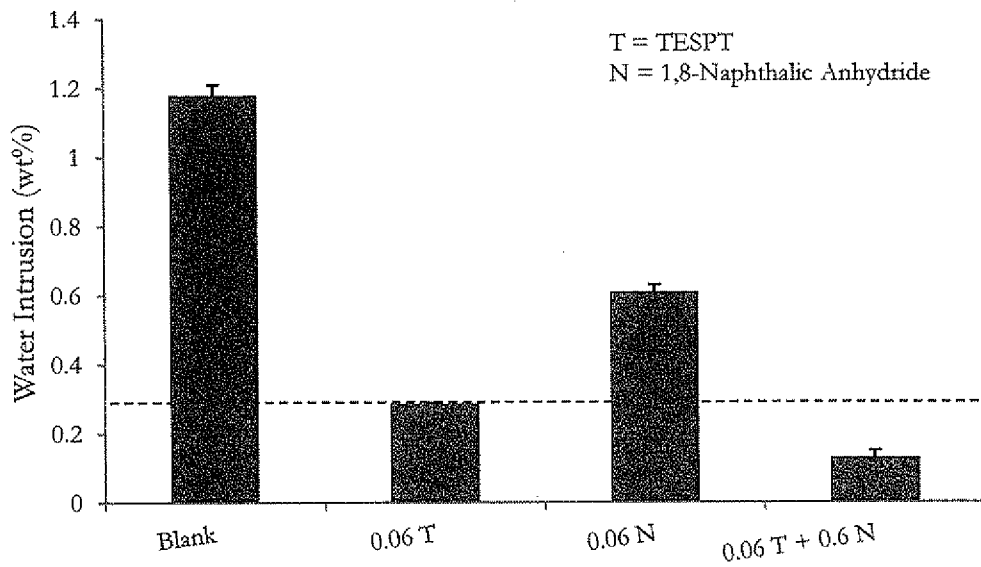


Figure 2

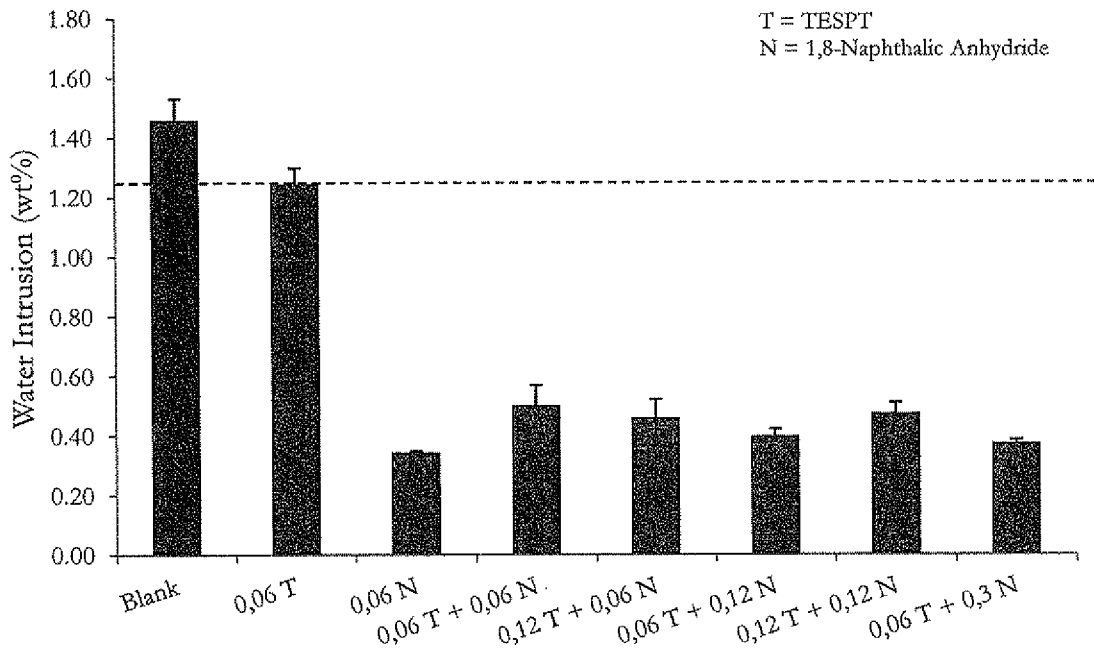
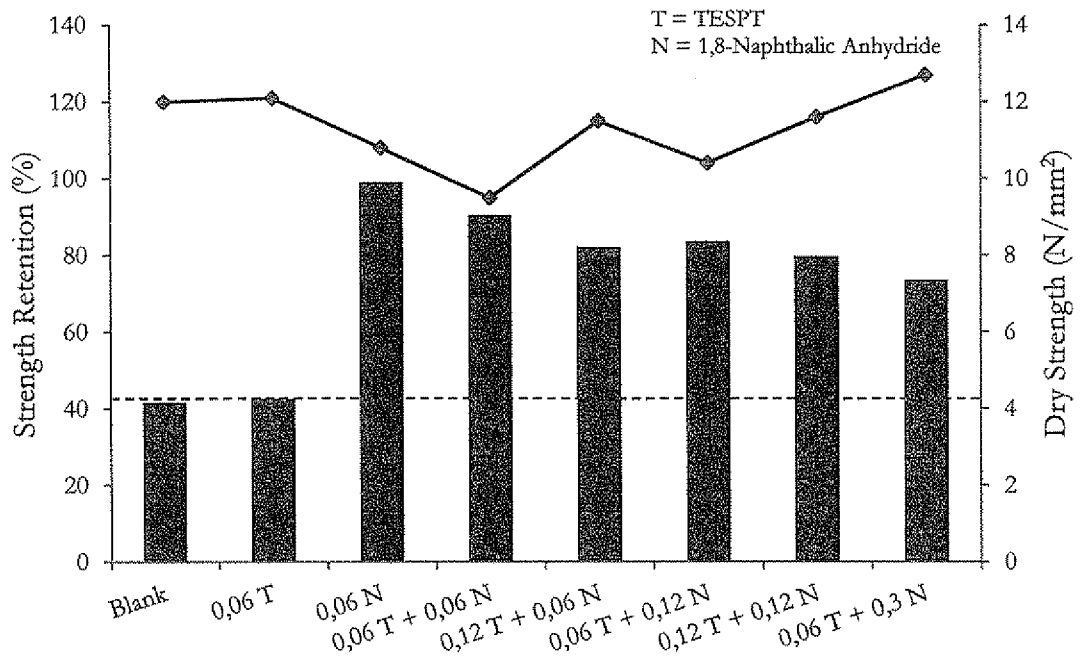


Figure 3



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/064742

A. CLASSIFICATION OF SUBJECT MATTER
INV. C04B12/00 C04B28/36 C04B28/26
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)
C04B
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 practicable, search terms used)
EPO-Internal, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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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

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"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 25 July 2013	Date of mailing of the international search report 05/08/2013
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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 Burtan, M
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/064742

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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