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(54) **Title:** FIRE RETARDANT FORMULATIONS

(57) **Abstract:** The present invention relates to compositions where a substrate is liable to catch fire such as bituminous products, paints, carpets or the like. The invention relates to a composition comprising 40-95 weight % of a substrate to be rendered fire resistant such as bituminous material or paint, carpets which substrate is mixed with 5-60 weight % of a fire retardant component. The invention relates to a fire retardant component comprising or being constituted of attapulgit, and a salt being a source of a blowing or expanding agent, where the attapulgit and the salt are electrostatically connected by mixing and subjecting the mixture of the two components to agitation. Also, the invention relates to compositions comprising 40-95 weight % of a substrate to be rendered fire resistant mixed with 5-60 weight % of a fire retardant according to claim 1 or 2, which fire retardant component is mixed with the substrate or coated onto the substrate or applied as a separate layer to the substrate. The composition might additionally comprise between 0 -60 weight % of 20 other materials functioning as filler, plasticizer or the like.



Fire retardant formulations

Field of invention

The present invention relates to compositions where a substrate is liable to catch fire such as bituminous products, paints, carpets or the like. The invention relates to a composition comprising 40-95 weight % of a substrate to be rendered fire resistant such as bituminous material or paint, carpets which substrate is mixed with 5-60 weight % of a fire retardant component.

Background of the invention

Attapulgite (often called palygorskite) is a crystalline hydrated magnesium aluminium phyllosilicate with chemical formula $\text{Si}_8\text{O}_{20}\text{Al}_2\text{Mg}_2(\text{OH})_2(\text{OH}_2)_4(4\text{H}_2\text{O})$. The particle size is on the nanometer scale with approximate diameter of 20-25 nm and the length range from several hundred to several thousand nanometers. The attapulgite clay is considered as nano-clay because of the fact that at least one dimension of the particle is in the nanometer range. This diameter to length specification provides very high aspect ratios and large surface area. The high aspect ratios characteristic of this mineral is comparable to carbon nanotubes. The rod-like fibrous structure gives the material a remarkable thermal and mechanical stability. The presence of relatively weak inter-rod interactions enables them to be easily blown-out or expand-out (due to the liberation of ammonia gas) resulting cross-linked char that swells under the release of ammonia gas from the blowing agent and behaves as expandable graphite or carbon nanotubes. Traditionally, attapulgite has found a wide range of applications such as suspending agent, reinforcing filler, improving mechanical properties and when attapulgite is added to liquids, attapulgite normally acts as a gelling agent or a carrier for an active component.

US patent application no. 2008/0141898 disclose mixing asphalt with a gelling agent such as attapulgite or other clay and further with thixotropic agents such as synthetic or organic fillers. It is suggested in paragraph [0027] that the asphalt might include aluminium trihydrate as a fire retardant, it is not suggested that attapulgite can be used as fire retardant. In the examples 1-14 an amount of 1-3 % attapulgite (MinUGel) is added to the asphalt.

US patent no. 3 730 890 disclose the use of attapulgite in combination with ammonium polyphosphate to produce a concentrate for an aerial fire retardant i.e. a liquid solution to be dropped on fires from planes. The attapulgite clay functions as a carrier in the liquid suspension, no chemical reaction takes place between the attapulgite and ammonium phosphate during preparation of the liquid solution.

US patent no. 8 686 073 discloses a flame or fire retardant composition containing mixtures of melamine polyphosphate with layered silicates added to polymer substrates such as polyamides. The flame retardant composition is used in plastic moulding compositions prepared by mixing the dry polymer substrate such as polyamide with a phenolic antioxidant and an amount of organo clay such as montmorillonite and possibly other additives. The mixture is heated to a temperature such as 220-250°C for polyamide in order to prepare a melt and then the melt is injected into a mould. The melamine polyphosphate and the layered silicates are not reacted prior to being added to the thermoplastic polymer substrate, the components are simply mixed with the substrate.

CN patent application no. 102352057 discloses a thermoplastic elastomer prepared by mixing 20-50 % ([0015]) of a flame retardant composite comprising attapulgite clay, melamin phosphate and cenospheres into an thermoplastic elastomer such as styrene compound (e.g., SBS, SIS, SEBS, SEPS), olefin compounds (TPO, TPV), diene compound (TPB, TPI), vinyl chloride-based compound (TPVC , TCPE), urethane-based compound (TPU), esters (TPEE), amide compound (TPAE), an organic fluorine compound (the TPF) and the like ([0018]). According to this disclosure attapulgite clay, melamine phosphate and cenospheres are mixed to a compound and the flame retardant effect of the three components complement and promote each other ([0012]). It is not suggested in CN102352057 that the components can be used individually in a thermoplastic elastomer and no examples illustrate the effect of using one or two of the components together in a flame retardant. The three components of the flame retardant does not react with each other during mixing, they are simply blended to form a composite. The three components are therefore not electrostatically connected, i.e. no chemical bonding is formed between the components.

Summary of the invention

The present invention was made in view of the prior art described above, and the object of the present invention is to provide an improved fire retardant and to provide a composition being less inclined to catch fire and being more inclined to self-extinguishing and further to provide methods for producing such fire retardant and compositions.

To solve the problem, the present invention provides the invention of independent claims 1 or 4.

According to a first aspect the present invention relates to a fire retardant component comprising or being constituted of:

- attapulgite, and
- a salt being a source of a blowing or expanding agent,

5 where the attapulgite and the salt are electrostatically connected i.e. are chemically bonded.

Normally, "electrostatically" means that the chemical bond is an ionic bond. The chemical bonding is normally obtained by subjecting the mixture of the two components to agitation for a time period adequate for chemical bonding to take place. The agitation may take place in an aqueous solution but can also be a dry mixing of attapulgite and a salt.

According to some embodiments of the first aspect, the attapulgite has been modified before mixing providing the surface of the attapulgite with hydroxyl groups. "Modified" might also be referred to as "surface active".

According to some embodiments of the first aspect, the fire retardant component comprises at least 20 weight % of attapulgite, and at least 20 weight % of the salt being a source of a blowing or expanding agent.

20 Optionally, the fire retardant may include other components e.g. one or more fire retardants or components improving mixing and/or reaction of the mixture, at least the components may not impact the preparation of the product or the effect of the final product negatively. Such further components can be present in amounts from 0-60 weight % and such a component might be melamine,

25 According to some embodiments, the salt is a source of a blowing or expanding agent comprising phosphor and nitrogen and might be chosen from ammonium polyphosphate, melamine phosphate, melamine coated ammonium polyphosphate or another polyphosphate or a mixture of the these salts.

30 According to a second aspect, the invention relates to a composition comprising or containing:

- 40-95 weight % of a substrate to be rendered fire resistant
- 5-60 weight % of a fire retardant component according to the first aspect, and
- 0-55 weight % of other materials functioning as filler, plasticizer or the like.

35 This content may be applied as a separate layer in a substrate or may be evenly distributed in the mass of the substrate. Optionally, the composition comprises less than 50 weight%, or even less than 35 weight% of the fire retardant according to the first aspect. The composition may normally comprises less than 20 weight %, even less than 15 weight% of other materials functioning as filler, plasticizer or the like.

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According to some embodiments of the second aspect, the fire retardant component is mixed with the substrate or coated onto the substrate possibly in a mixture with further components or applied as a separate layer to the substrate possibly in a mixture with further components. That the fire retardant is coated onto the substrate or applied as a separate layer to the substrate “possibly in a mixture with further components” means that the fire retardant can be mixed with other components e.g. providing strength, filling or other characteristics which mixture is then coated or applied onto the substrate.

According to some embodiments of the second aspect, the substrate is a material used to prepare layers fully or partly covering a surface, normally the layers have a thickness between 0.5 – 20 mm.

According to some embodiments of the second aspect, the substrate is liquified before application e.g. by heating or adding a solvent, and afterwards the substrate hardens or cures into a solid structure.

According to some embodiments of the second aspect, the substrate comprises a bituminous material e.g. a roofing material or the like.

According to some embodiments of the second aspect, the substrate is a layer of material used for interior or exterior decoration or insulation such as a carpet or a cover or the like, or the substrate is a liquid material used for interior or exterior application to buildings such as a paint or the like. According to these embodiments the fire retardant may be provided in a solution or dispersion and either coated onto the layer or mixed into the liquid material. If the solution is to be coated onto a layer, the solution or dispersion may comprise latex.

According to a third aspect, the invention relates to a method for manufacturing a fire retardant component according to the first aspect, wherein

- a homogeneous powder of attapulgite is mixed with a powder of the salt being a source of a blowing or expanding agent and optionally with an amount of liquid such as water or an aqueous solution,
- the mixture is blended and possibly grinded,
- after step b) the mixture is dried if necessary.

This method will normally result in a fire retardant component in form of a loose powder.

According to some embodiments of the third aspect, the attapulgite is made surface active optionally by treating the attapulgite with acid such as HCl during agitation or high-shearing in order to obtain a surface activated attapulgite prior to use in step a).

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According to some embodiments of the third aspect, the drying temperature in step c) is between 80-130°C.

According to a fourth aspect, the invention relates to a method for manufacturing a composition according to the second aspect to be rendered fire resistant, wherein a fire retardant component according to the first aspect is incorporated, where a mass defining the properties of the substrate to be rendered fire resistant is first provided, then either

- d1) optionally the substrate to be rendered fire resistant is pre-treated e.g. by softening or plasticizing it e.g. by subjecting to high-shear blending or adding a softener such as SBS or the like, to make the material fluid or at least soft and formable,
- e1) agitating and mixing the optionally pre-treated material with the dried powder of step c) of the third aspect, e.g. by high-shear blending
- or
- d2) the dried mixture of step c) of the third aspect is dispersed in a solvent until a desired viscosity is reached,
- e2) the dispersed fire retardant component is applied to a surface of the substrate in a layer either in a wet condition or in a dried condition as a separate layer.

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Brief description of the drawings

Figure 1 shows TEM image of nano-clay attapulgite

Figure 2 shows the structure of electrostatically bonded attapulgite-melamine coated ammonium phosphate

Figure 3 shows a TEM image of nano-clay attapulgite/MAPP complex

Figure 4 shows impregnated reinforcement using bitumen and fire retardant as main components before fire test.

Figure 5 shows impregnated reinforcement using bitumen and fire retardant as main components after fire test.

Figure 6 shows layers of a top layer of a roofing system.

Figure 7 shows layers of a base layer of a roofing system.

Figure 8 shows test results of industrial fire test of a roofing system with no fire retardant (reference) performed at 2m/s air velocity.

Figure 9 shows test results of industrial fire test of a roofing system with no fire retardant (reference) performed at 4m/s air velocity.

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Figure 10 shows test results of industrial fire test of a roofing system with fire retardant (sample) performed at 2m/s air velocity.

Figure 11 shows test results of industrial fire test of a roofing system with fire retardant (sample) performed at 4m/s air velocity.

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Detailed description of the invention

In describing the embodiments of the invention specific terminology will be resorted to for the sake of clarity. However, the invention is not intended to be limited to the specific terms so selected, and it is understood that each specific term includes all technical equivalents which operate in a similar manner to accomplish a similar purpose.

The fire retardant component of the invention has shown an excellent efficiency (synergism) towards inhibiting and/or stopping the combustion involved in the fire process. The fire retardant component works both in condensed phase as well as in gas phase.

The clay mineral i.e. the attapulgite is believed mainly to work in condensed phase as the clay mineral releases water upon heating and further act as thermal barrier for the substrate matrix.

A surface active or modified nano-clay such as attapulgite is provided with hydroxyl groups on the surface of the silicate. The surface active or modified nano-clay is normally provided with hydroxyl groups by treating the nanoclay such as attapulgite with an acid thereby generating hydroxyl groups i.e. silanol groups on the surface of the silicate, it might however be provided by other procedures.

That a salt is a source of a blowing or expanding agent means that the salt will develop so called non-flammable gas (ammonia gas behaves as non-flammable gas in the absence of a catalyst and at low concentration) or quenching radicals when subjected to fire. Normally the salt contains both phosphorous and nitrogen and the expanding agent NH_3 .

The salt can be a phosphorus-nitrogen containing polymer e.g. melamine coated ammonium polyphosphate and is believed to work mainly in condense phase and to trigger formation of phospho-carbonaceous and phospho-siliceous char after catalysing dehydration reaction of the phosphorous-nitrogen containing polymer. The released water being a result of dehydration reaction dilutes the combustible volatiles and slows down the high energy-production step in the fire.

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When describing the embodiments of the present invention, the combinations and permutations of all possible embodiments have not been explicitly described. Nevertheless, the mere fact that certain measures are recited in mutually different dependent claims or described in different embodiments does not indicate that a combination of these measures cannot be used to advantage. The present invention envisages all possible combinations and permutations of the described embodiments.

Preparing fire retardant component in powder form

10 Surface activation of attapulgite is achieved by treating the attapulgite with 4M HCl at 80 °C for 4 hours and subsequently washing the activated attapulgite with excessive deionized water until pH neutral. Figure 1 shows a Transmission Electron Microscopy (TEM) image of nano-clay attapulgite.

15 Ammonium polyphosphate (APP) and melamine coated ammonium polyphosphate (MAPP) was mixed with attapulgite (ATTP) in a ratio of ATTP/APP (1:3) and ATTP/MAPP (1:3) in two different vessels and stirred overnight at room temperature.

20 Next day, the mixtures were filtered and dried at 110°C for 24 hours and finally grinded in an ultra centrifugal mill ZM 200 with installed 80 µm sieve size in order to achieve maximum of 80 µm particle size.

25 Chemical structures and TEM images of a complex, ATTP-MAPP can be seen in figure 2 and 3 respectively. Figure 2 illustrates the complex resulting from the above process between attapulgite and the melamine coated ammonium polyphosphate.

Testing fire retardant mixed with bitumen

30 Table 1 disclose a first formulation for preparation of bitumen sheets. A fire retardant has been added to the formulation according to three different recipes. Colemanite is a hydrated calcium borate mineral presently used in bitumen sheets as a fire retardant and this mineral is therefore considered to be a standard for comparison purposes.

35 The recipe of the first formulation of bitumen sheet is, bitumen (74%) and SBS (Styrene Butadiene Styrene, 8%), SBS act as a plasticizer. The fire retardant according to recipe 9 is 18% mineral colemanite (reference) and the fire retardant according to recipe 17 is 18% ATTP-MAPP (inventive composition). However, recipe 15 contains only attapulgite mineral along with same amount of bitumen and
40 SBS used in other two recipes.

Table 1 Recipes of formulations with cone calorimetry results including time to ignition (TTI), peak heat release (PHR), total heat release rate (THRR) and mass loss.

Recipes	9 (reference)	15	17
	%	%	%
Bitumen	74	74	74
SBS	8	8	8
Colemanite	18		
ATTP		18	
ATTP-MAPP			18
TTI (s)	148	143	143
PHR (kW/10cm ²)	2,98	3,06	1,34
THRR (kJ/10cm ²)	516	265	229
Mass Loss (%)	60	40	25

- 5 Unmodified bitumen was melted on a burner at 215 °C followed by addition of SBS under high stirring at a rate of 10,000 rpm for 10 minutes. Subsequently, a fire retardant was added as defined in the above recipes at 200 °C at 1400 rpm for 10 minutes and further stirred the bitumen mixture for 25 minutes in order to get a homogenized mixture. The hot bitumen mixture was poured onto an aluminium
- 10 mould of size 25 cm x 10 cm x 0.25 cm (length x breadth x depth) and left for one hour to obtain room temperature. After one hour, the bitumen mixed fire retardant sheets were cut into 10 cm x 10 cm (length x breadth) size for cone calorimetry test and placed on a Rockwool carrier.
- 15 The fire retardancy results (cone calorimetry) of the first formulation (recipe 9, 15 and 17, Table 1) show that thermal stability of bitumen sheets according to recipe 17 is improved as total heat release rate (THRR) and peak heat release rate (PHR) for the bitumen prepared according to recipe 17 are around 2.24 times lower in compared to the bitumen prepared according to recipe 9.
- 20 The comparison of recipe 15 and 17 shows that mass loss rate is decreased due to the synergistic effect between attapulgite and melamine coated ammonium polyphosphate. Also, the PHR of the bitumen of recipe 17 is decreased significantly indicating that comparatively a smaller amount of fuel vapours are produced

resulting in less heat is released at specific interval of time and higher amount of phosphor-carbonaceous char is formed.

Preparation of bitumen sheets to mimic the production set-up

- 5 According to a second embodiment of the invention, a prepared fire retardant e.g. ATTP-MAPP-Melamine (20:60:20) being in powder form, can be dispersed in a solvent such as an aromatic oil (one of the component of bitumen) or bitumen and coated onto a reinforcement layer or sheet made of polyester and fibre glass, or provided as a separate thin adhesive sheet positioned under the bottom of a
10 bitumen sheet.

- In order to illustrate the effect of this embodiment, bitumen blend recipe containing 55 % bitumen and 45 % ATTP-MAPP-Melamine fire retardant was prepared and impregnated or coated on a standard carrier polyester and fibre glass
15 (reinforcement of size 100 cm length and 40 cm breadth) using a padder machine with installed two steel rollers. The space between two rollers was adjusted in such a way that on top of the reinforcement a layer (1.4 ± 0.1 mm) of the above bitumen fire retardant mixture was impregnated at constant speed and left for one hour at room temperature. On top of this impregnated reinforcement another layer of
20 almost same thickness containing bitumen 48 %, SBS 7%, CaCO_3 35% and 5 % ATTP-Melamine (30:70) was coated and left for overnight (figure 4).

Bitumen roofing system

- A bitumen roofing system is normally composed of 2 or 3 plies or layers each
25 comprising a reinforced bitumen membrane.

- A bitumen membrane comprises a reinforcement layer constituted of e.g. polyester, fiberglass or a composite carrier coated on both sides with bitumen. The applied bitumen is normally a modified bitumen indicating that the bitumen comprises
30 further components such as e.g. a polymer such as SBS or APP improving melt-behaviour and/or e.g. fire retarders.

- In each ply or layer the bitumen membrane is normally covered by other other layers providing desired characteristics such as a top surface layer providing UV-
35 protection and a weathering surface and a base layer providing adhesion to a either a lower ply or a substrate surface.

- Each ply or layer may include further layers providing e.g. insulation, fire protection or the like.

Standard Fire Testing

A standard test based on modified EN-1187 part 2 was performed.

5 The prepared samples were placed in a fire testing set-up on top of a Rockwool carrier and secured with two nails through the bitumen-reinforcement sheet. A dried
premade wooden crib was exposed to 5 propane flames (height ± 120 mm) for 30
seconds and ignited crib placed 100 mm away from the bottom of the bitumen-
reinforcement sheet. A constant airflow of 2 m/s with the help of an adjustable fan
was maintained during the test. The fire test lasted for 15 minutes unless until the
10 fire self-extinguished.

The extent of the damage on the bitumen-reinforcement sheets were measured starting from the centre of the wooden crib to the last damaged area near the top.

15 The fire test was performed on two samples and the variation between the samples was not more than 1 cm. The damage to the two samples was recorded 44 cm and 43 cm, respectively (figure 5). In order to pass the fire test, damage must not exceed 55 cm. The fire test was also performed on the standard bitumen-
reinforcement samples from the production plant containing no fire retardants in the
20 bitumen formulation. The fire test on the standard sample results a damage of 75 cm.

The conclusion is that blend recipes incorporated fire retardant (ATTP-MAPP and ATTP-MAPP-Melamine) either in the impregnated reinforcement or mixed into the
25 bitumen-SBS mixture has remarkable fire retardant effects. The bitumen-
reinforcement sheets containing fire retardant self-extinguished after 8 minutes as compared to the standard samples that continued to burn for 15 minutes and set off fire forcefully.

30 **Test and implementation of modified attapulgate for roofing**

This test procedure applies the standard ENV 1187-part 2. In order to test the fireretardant (FR) 142 rolls of bituminous sheets (length and width of one roll
~700cm*100cm, respectively) were produced. The FR was produced separately
and mixing of the FR into bitumen was done at the production plant.

35

A roofing system composed of two plies i.e. a base layer (first layer) and a top layer was produced and tested. The composition of the top layer and the base layer are shown in figure 6 and 7 respectively.

Two different base layers as illustrated in figure 7 were produced. A reference base layer where the layer “Impregnated reinforcement with and without FR” is constituted of a polyester/glass fleece coated with bitumen. The polyester/glass fleece traditionally both work as reinforcement and as fire retardant. According to a second embodiment the layer “Impregnated reinforcement with and without FR” of the base layer is constituted of standard reinforcement coated with a blend containing 75% oxidized bitumen and 25% FR. The FR comprises modified attapulgite (ATTP) + melamine coated ammonium polyphosphate (MAPP) + Melamine (20%-60%-20%).

Fire Testing (ENV 1187-part 2)

A standard fire test was performed in order to evaluate the efficiency of incorporated fire retardant with the reference product.

The result of such a test is expressed as a degradation length of the sample due to the flame at 2m/s and 4m/s air velocity. To pass the test, the degradation length has to be less than 65 cm from the bottom of the sample. See figure 8.

The results are shown in the table below:

Fire Test ENV 1187-part 2			
Test	Base layer with reinforcement	Degradation length (mm) 2m/s	Degradation length (mm) 4m/s
1	Reference	335/345/335	345/370/360
2	Sample	275/280/275	315/310/315

Conclusion

The degradation length for the test object including the new fire retardant is reduced compared to the degradation length of the reference object. The new fire retardant therefore gives comparatively better results than the existing system used within this field to reach good fire properties.

Claims

1. A fire retardant component comprising or being constituted of:
 - attapulgite, and
 - 5 - a salt being a source of a blowing or expanding agent,where the attapulgite and the salt are electrostatically connected i.e. are chemically bonded.
- 10 2. A fire retardant component according to claim 1, wherein the attapulgite is modified before mixing providing the surface of the attapulgite with hydroxyl groups.
- 15 3. A fire retardant component according to claim 1 or 2, comprising at least 20 weight % of attapulgite, and at least 20 weight % of a salt being a source of a blowing or expanding agent, and optionally 0-60 weight % of one or more components providing an effect as filler, fire retardant, mixing aid or other desired effect.
- 20 4. A fire retardant according to any previous claim, wherein the salt being a source of a blowing or expanding agent comprises phosphor and nitrogen and might be chosen from ammonium polyphosphate, melamine phosphate, melamine coated ammonium polyphosphate or another polyphosphate or a mixture of the these salts.
- 25 5. A composition comprising or containing:
 - 40-95 weight % of a substrate to be rendered fire resistant
 - 30 - 5-60 weight % of a fire retardant component according to one of claims 1-4, and
 - 0-55 weight % of other materials functioning as filler, plasticizer or the like.
- 35 6. A composition according to claim 5, wherein the fire retardant component is mixed with the substrate or coated onto the substrate possibly in a mixture with further components or applied as a separate layer to the substrate possibly in a mixture with further components.
7. Composition according to any one of claims 5-6, wherein the substrate is a material used to prepare layers fully or partly covering a surface, normally the layers have a thickness between 0.5 – 20 mm.
- 40 8. Composition according to any one of claims 5-7, wherein the substrate can be liquified before application e.g. by heating or adding a solvent, and afterwards the substrate hardens or cures into a solid structure.

9. Composition according to any one of claims 5-8, wherein the substrate comprises a bituminous material.

5 10. Composition according to any one of claims 5-8, wherein the substrate is a layer of material used for interior or exterior decoration or insulation such as a carpet or a cover or the like, or the substrate is a liquid material used for interior or exterior application to buildings such as a paint or the like.

10 11. Method for manufacturing a fire retardant component according to one of the claims 1-4, wherein
a) a homogeneous powder of attapulgite is mixed with a powder of the salt being a source of a blowing or expanding agent and optionally with an amount of liquid such as water or an aqueous solution,
b) the mixture is blended and possibly grinded,
15 c) after step b) the mixture is dried.

12. Method according to claim 11, wherein the attapulgite is made surface active e.g. by treating the attapulgite with acid such as HCl during agitation or high-shearing in order to obtain a surface activated attapulgite prior to use in step a).

20 13. Method according to any of the claims 11-12, wherein the drying temperature in step c) is between 80-130°C.

14. Method for manufacturing a composition according to any one of claims 5-10 to be rendered fire resistant, wherein a fire retardant component according to one of claims 1-4 is incorporated, where a mass defining the properties of the substrate to be rendered fire resistant is first provided, then either

25 - d1) optionally the substrate to be rendered fire resistant is pre-treated e.g. by softening or plasticizing it e.g. by subjecting to high-shear blending or adding a softener such as SBS or the like, to make the material fluid or at least soft and formable,

30 - e1) agitating and mixing the optionally pre-treated material with the dried powder of step c) of any of claims 11-12, e.g. by high-shear blending
or

35 - d2) the dried mixture of step c) of any of claims 11-12 is dispersed in a solvent until a desired viscosity is reached,

- e2) the dispersed fire retardant component is applied to a surface of the substrate in a layer either in a wet condition or in a dried condition as a separate layer.

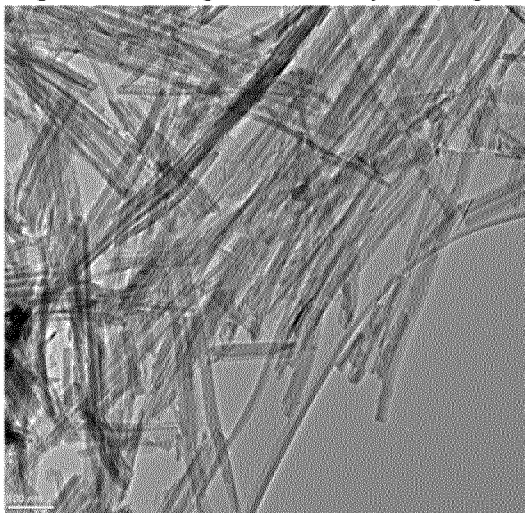
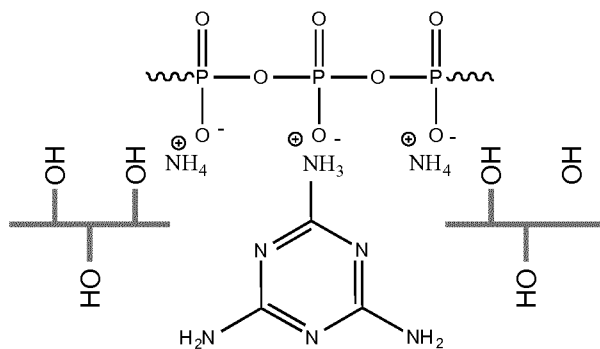
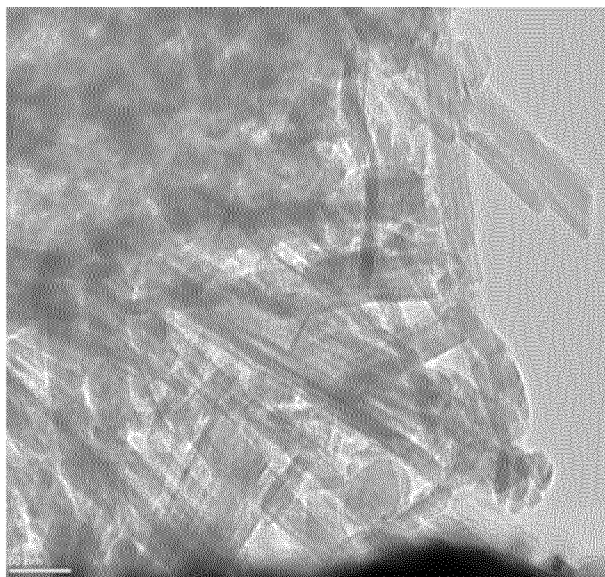
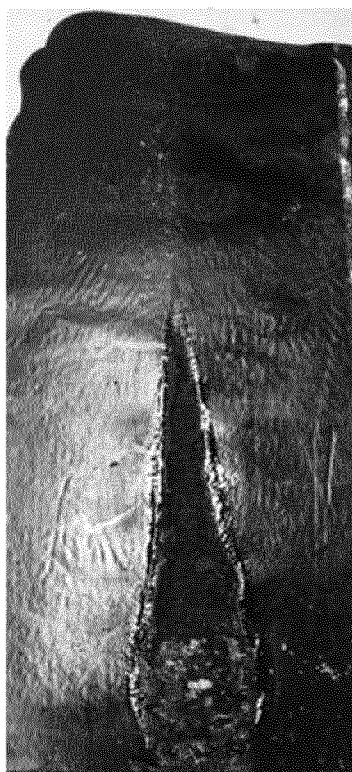
Fig. 1. TEM image of nano-clay attapulgite**Fig. 2.** Electrostatically bonded attapulgite-melamine coated ammonium phosphate**Fig. 3.** TEM image of nano-clay attapulgite/MAPP complex

Fig. 4: Example of bitumen-reinforcement sample with fire retardant – before fire test



Fig. 5: Example of bitumen-reinforcement sample with fire retardant - after fire test.



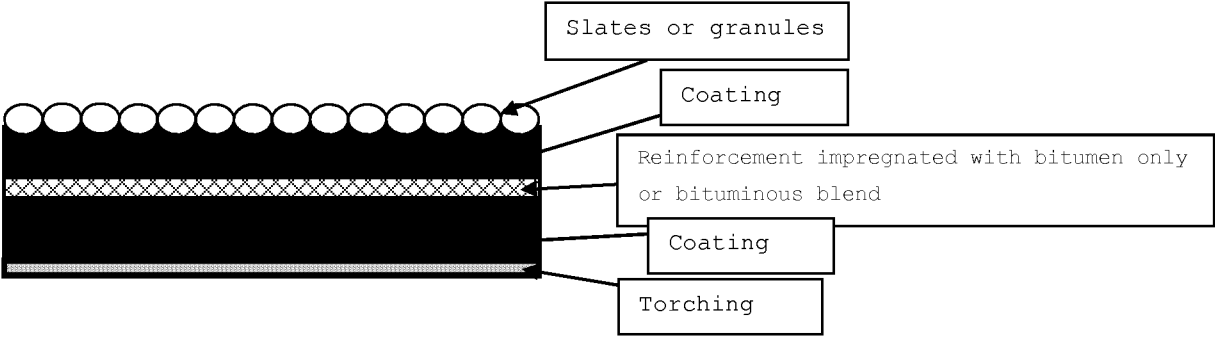


Figure 6

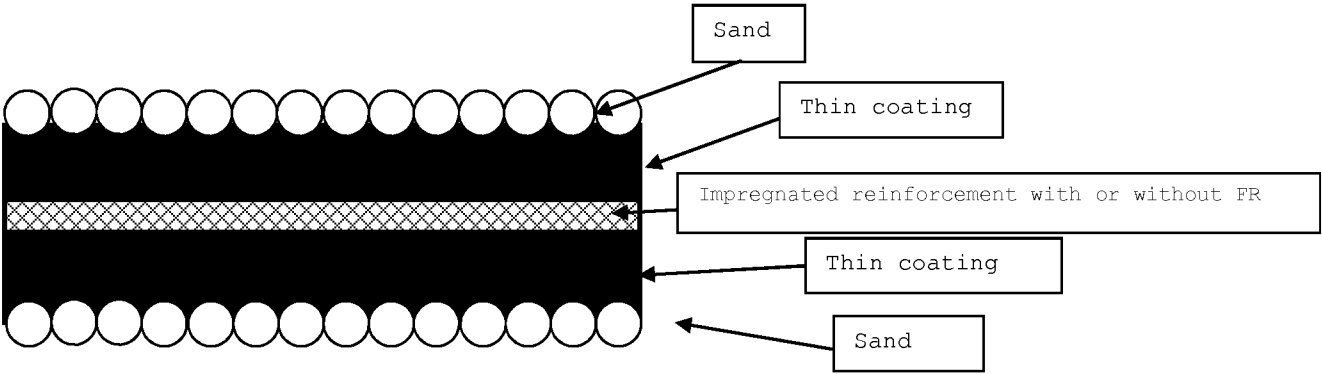


Figure 7

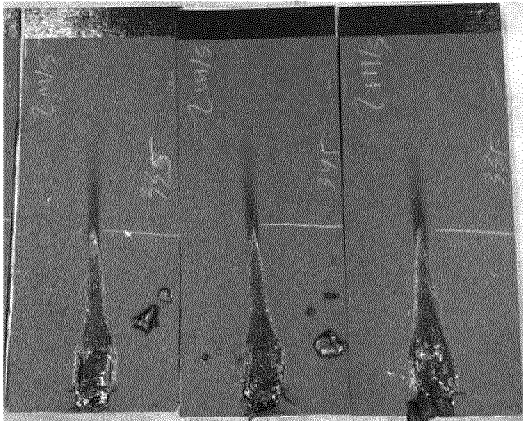


Figure 8

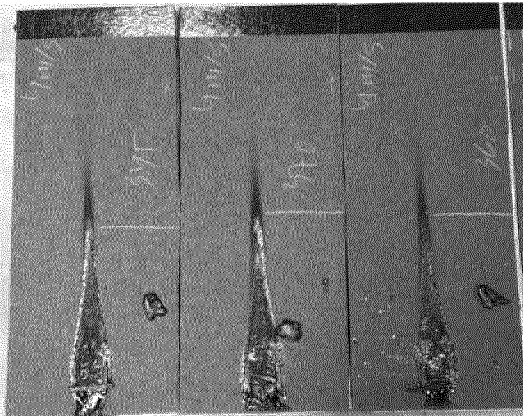


Figure 9



Figure 10

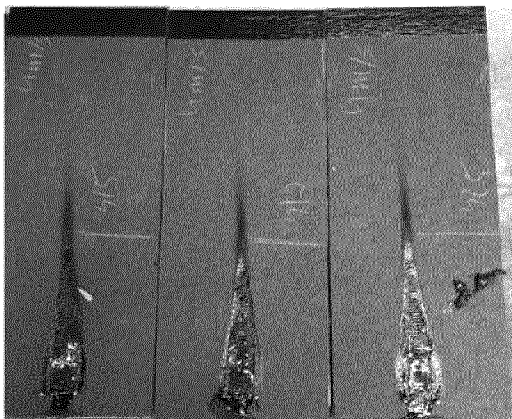


Figure 11

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/064978

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K21/04 C09K21/12
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)
C09K

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 102 352 057 A (UNIV NORTHWEST NORMAL) 15 February 2012 (2012-02-15) the whole document	1-14
A	US 2014/336318 A1 (ESTEBAN CUBILLO ANTONIO [ES] ET AL) 13 November 2014 (2014-11-13) paragraphs [0001], [0011] - [26.54.55.78] claims; examples	1-14
A	US 2002/096668 A1 (VANDERSALL HOWARD L [US] ET AL) 25 July 2002 (2002-07-25) the whole document	1,11
A	US 3 730 890 A (NELSON K) 1 May 1973 (1973-05-01) cited in the application the whole document	1,11
	-/--	



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

29 August 2016

Date of mailing of the international search report

05/09/2016

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2016/064978

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2008/141898 A1 (FIELDS JOHN R [US]) 19 June 2008 (2008-06-19) cited in the application the whole document	1-14
A	----- US 2013/165558 A1 (PFAENDNER RUDOLF [DE] ET AL) 27 June 2013 (2013-06-27) the whole document -----	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/064978

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 102352057	A	15-02-2012	NONE

US 2014336318	A1	13-11-2014	EP 2796492 A1 29-10-2014
			ES 2415241 A1 24-07-2013
			JP 5965495 B2 03-08-2016
			JP 2015509069 A 26-03-2015
			US 2014336318 A1 13-11-2014
			WO 2013093139 A1 27-06-2013

US 2002096668	A1	25-07-2002	AU 1663202 A 11-06-2002
			AU 2002216632 B2 12-01-2006
			CA 2430420 A1 06-06-2002
			EP 1343855 A2 17-09-2003
			ES 2415835 T3 29-07-2013
			ES 2540084 T3 08-07-2015
			US 2002096668 A1 25-07-2002
			WO 0244305 A2 06-06-2002

US 3730890	A	01-05-1973	AR 193301 A1 11-04-1973
			ES 409222 A1 16-12-1975
			FR 2162205 A1 13-07-1973
			US 3730890 A 01-05-1973
			ZA 7208508 B 29-08-1973

US 2008141898	A1	19-06-2008	CA 2522448 A1 07-04-2006
			US 2008141898 A1 19-06-2008

US 2013165558	A1	27-06-2013	CN 102257070 A 23-11-2011
			EP 2379643 A1 26-10-2011
			JP 2012512300 A 31-05-2012
			JP 2014062272 A 10-04-2014
			US 2011269880 A1 03-11-2011
			US 2013165558 A1 27-06-2013
			WO 2010069835 A1 24-06-2010
