A FIRE PERFORMANCE MATERIAL, AND CABLE INCLUDING THE MATERIAL

Abstract: A fire resistant material including an extrudable mixture of an silicone elastomer or polymer 1.006 including silicon and CaCO₃ filler 1.004, the CaCO₃ filler being present in the mixture in amount to leave an insulating or protective layer 1.012 on a substrate such as an electrical conductor 1.010. The material contains no more than 50 parts by weight of ceramizable or glassforming filler to 100 parts by weight polymer. The silicone polymer and CaCO₃ in combination preferably form more than 92% of the material. When used as a layer or jacket for a cable, the mixture decomposes on exposure to fire to provide a protective or electrically insulative layer on the conductor.
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A fire performance material, and cable including the material

Field of the invention

[001] This invention relates to a fire performance composition or material, a cable insulated with the material, and to a method of manufacturing a cable using the composition.

[002] The invention is particularly suited for use in fire resistant cables and other applications where composition is required to maintain physical and/or electrical characteristics during and after exposure to fire.

Background of the invention

[003] Flame retardant cable jackets are known in which additives are added to the plastics material to counter the fire by producing, for example, water or carbon dioxide. Additives can include aluminium hydroxide, as discussed in US6043309 (Dow Corning) which is addressed to improvements in the extrusion properties and viscosity of silicone with aluminium hydroxide.

[004] GB2016307 (AEI) discloses a mineral insulated electrical cable having a water repellent filling. Such cables consist of an electrical conductor contained in a hollow metal jacket, with a powdered filler material contained between the conductor and the jacket. The filler can include a silicone material. This document does not disclose a cable jacket material having a flexible jacket of silicone with a filler material blended into the silicone jacket material. The powdered filler cannot be applied by extrusion.

[005] EP0283132 (AEI) discloses a mineral insulated electrical cable having a filling which included flame retardant and water repellent characteristics. The structure of these cables is an electrical conductor contained in a metal jacket, with the filler material in powdered form and compacted between the conductor and the jacket. The powder filler can include, among other materials, CaCO\textsubscript{3} in proportions of up to about 5\%, and the water resistant material can be, among other materials, silicone in either a liquid or powder form. The CaCO\textsubscript{3} is included for the purpose of generating CO\textsubscript{2}. This document
does not disclose a cable jacket material having a flexible jacket of silicone with a filler material blended into the jacket material. The low proportion of CaCO$_3$ would not permit the formation of a useful or significant post-combustion residue.

[006] EP0708455 (Datwyler) discloses a flame resistant material including an organosilicon polymer with a ceramizable filler material. This specification describes a number of ceramizable fillers or glassformers, being a material that has the property of being able to form a glass, or an amorphous liquid with very high viscosity at room temperature but with low viscosity at high temperatures as seen in a fire. Additional auxiliary fillers, such as CaCO$_3$, among others, are also disclosed, for use in addition to the ceramizable filler. The purpose or function of these additional fillers is not disclosed. Ceramizable fillers are an essential component of EP0708455. At [4,7] the specification states that the organosilicon material needs to be compatible with the ceramizable filler. The specification discloses between 50 and 300 parts by weight of ceramizable filler per 100 parts by weight of polymer. An upper limit of 500 parts by weight of ceramizable and non-ceramizable filler is disclosed. The EP0708455 specification indicates that materials according to the invention all contain a ceramizable composition in the proportions set out above, the purpose being to produce a post-combustion ceramic layer on the wires. However, EP0708455 discloses only a material with amounts of ceramizable filler sufficient to form an insulative layer. EP0708455 does not disclose or suggest a material without any ceramizable filler or with amounts of ceramizable filler insufficient to form a useful insulation layer. The minimum amount of ceramizable filler disclosed is 50 parts by weight of ceramizable filler to 100 parts by weight of polymer.

[007] It is also known to wrap mica impregnated tapes around a conductor to improve its fire resistance. However, this process is slow and costly.

[008] It is desirable to provide a fire performance material and a fire performance cable which is simple and cost effective to manufacture.

Summary of the invention

[009] The invention is predicated, at least in part, on the inventor's insight that certain compounds of calcium, silicone, and oxygen have high electrical resistivity. In
addition, at least some of such compounds may also have good mechanical properties such as strength, cohesiveness and adhesion to metal.

[010] According to one embodiment of the invention a fire performance material including a polymer (1.006) including silicone polymer, and CaCO₃ filler (1.004), wherein the CaCO₃ filler is present in the material in an amount to leave a post-combustion residue after exposure of said material to fire, the material including less than 50 parts by weight of ceramizable filler to 100 parts by weight of polymer.

[011] The post-combustion residue can be an insulating residue or a protective residue.

[012] The material can advantageously include less than 20 parts by weight of ceramizable filler, preferably less than 10 parts by weight of ceramizable filler, preferably less than 5 parts by weight of ceramizable filler, and more preferably zero parts by weight of ceramizable filler.

[013] The ceramizable filler, defined in the background of the invention, can be those described in EP0708455.

[014] In one embodiment, not less than 92 weight % of the material can be made up of CaCO₃ and polymer.

[015] According to another embodiment of the invention, the fire performance material including at least 20 parts by weight CaCO₃ filler to 100 parts by weight of polymer.

[016] The CaCO₃ filler can be up to 250 parts by weight to 100 parts by weight of polymer.

[017] Preferably, the filler can be in the range of 30 parts by weight to 70 parts by weight filler to 100 parts by weight polymer.

[018] The silicone polymer of said fire performance material can be silicone elastomer.

[019] The polymer can consist exclusively of silicone elastomer.

[020] The fire performance material can further include a cross-linking agent.
The invention also includes a cable having a fire resistant layer made from the fire performance material. Said layer can be an insulating layer or a protective layer (jacket).

On exposure to flame, the insulating or protective layer can form a residue in the form of a post-combustion layer on a substrate. Said substrate can be one or several metal conductor, and/or one or several insulated conductor.

The residue can include at least one compound including Ca and Si.

The residue can include at least one of: Wollastonite (CaSiO₃), Calcium Oxide (CaO), Larnite (Ca₂(SiO₄)), Calcite (CaCO₃), Calcium Silicate (Ca₂SiO₄), Portlandite (Ca(OH)₂), SiO₂ (Hexagonal), and SiO₂.

The post-combustion residue can adhere to the conductor.

The residue can be cohesive.

The fire performance material can be applied as a jacket or sub-layer on an electrical conductor.

The material can be used to provide a coating on cable conductors.

The coating can be an external jacket or an internal layer.

The invention also provides a method of manufacturing a cable according to claim 11 including the steps of: mixing CaCO₃ filler (1.004) with the polymer (1.006) to obtain a coating material; and extruding the coating material onto an electrical conductor (1.010) to form the fire resistant layer (1.014).

The material of the present invention has the surprising advantage that a residue with good post-combustion electrical resistance characteristics is formed with little or no other fillers, and especially with little or no ceramifying material. At the same time, the material is cheaper than silicone polymer or silicone polymer and ceramifying filler.
Brief description of the drawings

[032] An embodiment or embodiments of the present invention will now be described, by way of example only, with reference to the accompanying drawings, in which:

[033] Figure 1 schematically illustrates the components of a cable coating system adapted to use the fire resistant material of the invention.

[034] Figure 2 is a graphical representation of X-Ray Diffraction analysis of the post-combustion residue according to an embodiment of the invention.

[035] The numbering convention used in the drawings is that the digits in front of the full stop indicate the drawing number, and the digits after the full stop are the element reference numbers. Where possible, the same element reference number is used in different drawings to indicate corresponding elements.

Detailed description of the embodiment or embodiments

[036] The invention will be described in the context of a cable coated with material according to an embodiment of the invention, and with reference to the drawings.

[037] As mentioned above, certain compounds of calcium, silicon, and oxygen, such as Wollastonite (CaSiO₃), have good electrical resistivity. Wollastonite has a melting point in excess of 1500°C.

[038] The invention derives in part from the inventor's insight that such compounds may be formed during combustion by providing potential precursor material for calcium oxide and silica from silicone decomposition. The inventor deduced that a mixture of silicone and CaCO₃ in the presence of fire can produce the CaO and silica, which would then become available to form the target compounds during the fire. The inventor further reasoned that the mechanical properties of such combustion products could be sufficient to provide an insulative or protective residue which has adequate mechanical properties such that ceramic forming fillers were thus superfluous at least for some applications.
Accordingly, one embodiment of the invention provides a fire resistant material including a mixture of silicone polymer and CaCO₃, the CaCO₃ being present in the mixture in an amount to leave an insulating or protective layer on a substrate such as an electrical conductor.

Products of the exposure of the mixture of silicone elastomer and CaCO₃ can include one or more of the following: Wollastonite (CaSiO₃), Calcium Oxide (CaO), Larnite (Ca₂(SiO₄)), Calcite (CaCO₃), Calcium Silicate (Ca₂SiO₄), Portlandite (Ca(OH)₂), SiO₂ (Hexagonal), and SiO₂ (Rhombo. H. axes) in a mix of crystalline and amorphous forms. The resulting post-combustion residue provides surprisingly good electrical properties at temperatures of the order of 1000°C.

Figure 1 schematically illustrates the components of a cable coating system adapted to use the fire resistant material of the invention.

The system includes a supply of CaCO₃ 1.004, a supply of silicone elastomer 1.006, a mixer 1.008, and an extruder head 1.012.

The CaCO₃ and silicone elastomer are mixed in the mixer 1.008 in a predetermined ratio to provide an extrudable composition and fed to the extruder 1.012. A single electrical conductor, or a bundle of electrical conductors, 1.010 is drawn through the extruder head and coated with the mixture. The mixture is such as to form an electrical insulating layer 1.014 on the conductor, the insulating layer having adequate mechanical properties to permit the handling, installation and use of the cable, and such that, after exposure to fire, the combustion products of the mixture will form an electrically resistive or insulative residue layer to maintain electrical functionality of the cable.

An additional external jacket can be extruded over the layer of fire resistant material to provide additional strength or insulation if required.

Example 1

A sample consisting of CaCO₃ (Omyacarb 2T) to Wacker R40 1/80S silicone elastomer (50/50 wt% basis) with 2% Perkadox 14-40 peroxide as a cross-linking
agent was prepared and subjected to controlled heating, the resulting residue was then analysed.

047 The composition was prepared by adding CaCO$_3$ (Omyacarb 2T) (50/50 wt% basis) to Wacker R401/80S silicone elastomer with 2% Perkadox 14-40 peroxide.

048 The composition was extruded at 0.8 mm wall thickness onto 7/0.50 mm bunched plain annealed copper wire and air oven cured at 190°C/2hrs.

049 The coated wire was twisted with another coated wire and subjected to a fast rising temperature in a tube furnace while measuring the resistance between the twisted wires.

050 The results show that the resistance at 1000°C ranges between 0.5 MΩ and 1.13 MΩ. None of the Silicone-CaCO$_3$ combinations resulted in a cable that had zero resistance (i.e. failed to 0 Ω) for the single layer.

051 A powder sample of the residue was subjected to X-Ray Diffraction analysis to determine its phase composition. A Bruker D8 Advance X-ray Diffractometer with CuK$_0$ radiation (40kV, 40mA) monochromatised with a graphite sample monochromator was employed to determine the X-ray diffraction (XRD) pattern. The sample was scanned over the 2-theta range 5° to 85° with a step size of 0.02° and a count time of 4 seconds per step. Analyses were performed on the collected XRD data for the sample using the Bruker XRD search match program EVA™.

052 Crystalline phases were identified using the ICDD-JCPDS powder diffraction database. A variety of phases were identified as shown in Figure 2.

053 Analysis showed that heating of the CaCO$_3$ and silicone to 1000°C produces a number of compounds including Wollastonite (CaSiO$_3$), Calcium Oxide (CaO), Larinite (Ca$_2$(SiO$_4$)$_{2/3}$), Calcite (CaCO$_3$), Calcium Silicate (Ca$_2$SiO$_4$), Portlandite (Ca(OH)$_2$), SiO$_2$ (Hexagonal), and SiO$_2$ (Rhombo.H. axes) in a mix of crystalline and amorphous forms.

054 Test showed that the residue exhibited resistivities between 0.5 MΩ and 1.13 MΩ.
Figure 2 illustrates X-Ray Diffraction analysis results for the residue from mixture according to an embodiment of the invention. Peaks can be seen for Larnite, Wollastonite, CaO (Face Centred), and Calcite.

An advantage of the present invention is that silicone can be heavily loaded with CaCO₃. A range of 20% to 70% CaCO₃ and 80% to 30% silicone may be possible. This provides a cost advantage in that CaCO₃ is significantly cheaper than silicone. Both the pre-combustion mixture and the post-combustion residue have good electrical insulative properties. The post combustion residue also has good adhesion to the conductor and good mechanical strength. The residue layer can also serve to protect the conductor from water.

In this specification, reference to a document, disclosure, or other publication or use is not an admission that the document, disclosure, publication or use forms part of the common general knowledge of the skilled worker in the field of this invention at the priority date of this specification, unless otherwise stated.

In this specification, terms indicating orientation or direction, such as "up", "down", "vertical", "horizontal", "left", "right" "upright", "transverse" etc. are not intended to be absolute terms unless the context requires or indicates otherwise. These terms will normally refer to orientations shown in the drawings.

Where ever it is used, the word "comprising" is to be understood in its "open" sense, that is, in the sense of "including", and thus not limited to its "closed" sense, that is the sense of "consisting only of. A corresponding meaning is to be attributed to the corresponding words "comprise", "comprised" and "comprises" where they appear.

It will be understood that the invention disclosed and defined herein extends to all alternative combinations of two or more of the individual features mentioned or evident from the text. All of these different combinations constitute various alternative aspects of the invention.

While particular embodiments of this invention have been described, it will be evident to those skilled in the art that the present invention may be embodied in
other specific forms without departing from the essential characteristics thereof. The present embodiments and examples are therefore to be considered in all respects as illustrative and not restrictive, and all modifications which would be obvious to those skilled in the art are therefore intended to be embraced therein.
Claims

1. A fire performance material including a polymer (1.006) including silicone polymer, and CaCO₃ filler (1.004), characterized in that the CaCO₃ filler is present in the material in an amount to leave a post-combustion residue after exposure of said material to fire, the material including less than 50 parts by weight of ceramizable filler to 100 parts by weight of polymer.

2. A fire performance material as claimed in claim 1, characterized in that it includes at least 20 parts by weight CaCO₃ filler to 100 parts by weight of polymer in the material.

3. A fire performance material as claimed in claim 1 or claim 2, characterized in that the material has zero parts by weight of ceramizable filler.

4. A fire performance material as claimed in any one of the preceding claims, characterized in that it includes up to 250 parts by weight CaCO₃ filler to 100 parts by weight of polymer in the material.

5. A fire performance material as claimed in any one of the preceding claims, characterized in that it includes a range of 30 parts by weight to 70 parts by weight CaCO₃ filler to 100 parts by weight of polymer in the material.

6. A fire performance material as claimed in any one of the preceding claims, characterized in that the silicone polymer is silicone elastomer.

7. A fire performance material as claimed in any one of the preceding claims, characterized in that it further includes a cross-linking agent.

8. A fire performance material as claimed in any one of the preceding claims, characterized in that the residue includes at least one compound including Si and Ca.

9. A fire performance material as claimed in any one of the preceding claims, characterized in that the residue is cohesive.

10. A fire performance material as claimed in any one of the preceding claims, characterized in that not less than 92 weight % of the material is made up of CaCO₃ and polymer.
11. A cable having a fire resistant layer made from a fire performance material as claimed in any one of the preceding claims.

12. A method of manufacturing a cable according to claim 11, characterized in that the method includes the steps of:
mixing CaCO₃ filler (1.004) with the polymer (1.006) to obtain a coating material; and extruding the coating material onto an electrical conductor (1.010) to form the fire resistant layer (1.014).

14. A fire performance material substantially as herein described with reference to the accompanying drawings.

15. A cable substantially as herein described with reference to the accompanying drawings.
### INTERNATIONAL SEARCH REPORT

**International application No**

PCT/IB2010/000628

#### A. CLASSIFICATION OF SUBJECT MATTER

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

#### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08L C09D C08K HOIB

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

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

EPO-Internal, WPI Data

#### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C

See patent family annex

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

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Name and mailing address of the ISA/Authorized officer

European Patent Office P B 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel (+31-70) 340-2040, Fax (+31-70) 340-3016

Dalet, Pierre
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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

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