

(19)



(11)

EP 2 740 716 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

11.06.2014 Bulletin 2014/24

(51) Int Cl.:

C04B 35/00 (2006.01)

C08J 5/12 (2006.01)

C08J 5/18 (2006.01)

C08G 77/04 (2006.01)

C08L 83/04 (2006.01)

(21) Application number: **13460078.2**

(22) Date of filing: **26.11.2013**

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**

Designated Extension States:

BA ME

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(30) Priority: **29.11.2012 PL 40181012**

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(54) **Application of hybrid systems MgO-SiO₂ / multiwalled oligomeric silsesquioxanes as promoters of ceramization in silicone composites for covers of electrical cables**

(57) The invention solves the problem of application of the hybrid systems MgO•SiO₂/multiwalled oligomeric silsesquioxanes as promoters of ceramization in the silicone composites destined for covers of electrical cables. The systems are composed of magnesium silicate and

from 0.1 to 50 weight parts, favourably 10 weight parts, of the silsesquioxanes containing R₁ - R₈, where R₁ to R₈ is alkyl-group and/or groups, or alkoxy-, or methacryloxy-, or glycidoxo-, or amino-, or vinyl-, or perfluoro- or their mixture, used for its modification.

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Description

[0001] The subject of invention is application of hybrid systems $MgO \cdot SiO_2$ / multiwalled oligomeric silsesquioxanes as promoters of ceramization in silicone composites destined for covers of electrical cables.

[0002] Application of silicone composites containing inorganic particles, undergoing ceramization on fire, is commonly known in the cable industry. It is aimed to produce fire resistant electrical cables, which are able to provide electricity supply to electrical circuits and receivers during fire. They can find use in buildings or other objects of higher fire requirements therefore ensure increased safety during fire.

[0003] Such composites are made of silicone elastomers filled with pyrogenic silica. They are able to thermal vulcanization under the influence of organic peroxides, antyrenes and metallic or mineral compounds being ceramically active at high temperature.

[0004] Promoters and activators of ceramization process are very important components of ceramizable silicone composites, responsible for initiation and support of ceramic skeleton formation, which preserves cable cover from destruction during fire. With increasing temperature, organic parts of polymer phase degrade and ceramically active components of mineral phase are not able to assure expected mechanical strength of the material only by adhesion forces.

[0005] Activity of promoters and precursors plays also an important role in the rate of ceramic layer formation of the cable cover. According to actual state-of-the art it should meet expected mechanical properties at the temperature of 900 - 1100°C and no later than after 60 s.

[0006] The high rate of ceramization of the composite material makes thereby the outer, formed under high temperature, ceramic layer of cable cover, very effective in thermal insulation. It positively affects the sustainability of the physical properties of the cover and formation of ceramic layer of advantageous mechanical properties, what results in prolonged functionality of electrical cables on fire or the action of high temperature.

[0007] Application of fine particles silica as a precursor of ceramization is known from the publication "Ceramic - modified elastomers", published in Current Opinion in Solid State and Materials Science 1999, vol. 4, pp. 565 - 570, by J.E. Mark. However, use of silica nanoparticles brings about some technical limitations associated with high cost of their production and problems of dispersion in non-polar silicone polymer phase.

[0008] Able to oxidation compounds of magnesium, chemically reacting at high temperature with silica and/or aluminum compounds and producing such minerals as forsterite (Mg_2SiO_4), magnesium silicate ($MgSiO_3$), cordierite ($2Mg \cdot 2Al_2O_3 \cdot 5SiO_2$), spinel ($MgAl_2O_4$), which are the components of the ceramic outer layer formed, are known from the patent declaration US 2009/0099289. Important drawback of the above solution concerns the fact, that magnesium oxide, produced in high temperature oxidation of magnesium compounds, should quantitatively react up with silica and/or other components of mineral phase. Otherwise, the unreacted magnesium oxide left can adversely affect electrical insulation properties of cable cover.

[0009] The above problem does not occur if, products of hydrolysis of phenyltrichlorosilane ($C_6H_5SiCl_3$) and methyltrichlorosilane (CH_3SiCl_3), synthesized by known methods - described in the patent declaration P-397997, are used as precursor of ceramization.

[0010] In the patent declaration P-397998, another precursor of ceramization, namely tetraethoxysilane adsorbed on the surface of diatomite powder, has been presented. At the temperature of $120 \pm 10^\circ C$, under the influence of water contained in diatomite powder, rapid hydrolytic destruction of tetraethoxysilane occurs, resulting in highly reactive nanosilica particles formation on the surface of diatomite particles. Simultaneously an excess of moisture and ethanol, produced in the hydrolysis reaction, is evaporating.

[0011] Hybrid systems composed of silicate base and from 0.1 to 50 weight parts, preferably 10 weight parts, of silsesquioxanes containing $R_1 - R_8$, where R_1 to R_8 is alkyl- group and/or groups, or alkoxy-, or methacryloxy-, or glycidoxo-, or amino-, or vinyl-, or perfluoro- or their mixture, are known from the Polish patent declaration P-394903. They are synthesized by chemical functionalization of the filler surface with alkoxysilanes, followed by mechanical and chemical modification.

[0012] The essence of the invention is application of the hybrid systems $MgO \cdot SiO_2$ /multiwalled oligomeric silsesquioxanes, in silicone composites containing magnesium silicate and from 0.1 to 50 weight parts of the silsesquioxanes containing $R_1 - R_8$, where R_1 to R_8 is alkyl- group and/or groups, or alkoxy-, or methacryloxy-, or glycidoxo-, or amino-, or vinyl-, or perfluoro- or their mixture, used for its modification, as promoters of ceramization in the silicone composites destined for covers of electrical cables.

[0013] Application of the above mentioned hybrid systems makes possible to obtain a composite mix of high susceptibility to ceramization, which is able to produce well developed ceramic layer, effectively protecting metal wire of electrical cable from heat transfer and possible melting during fire.

Example no. 1

[0014] 40 weight parts of pyrogenic silica, having the specific surface area of 200 m²/g and platinum catalyst in the

form of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane are admixed to 100 weight parts of dimethyl-vinyl silicone of average molecular weight $M_w = 680\,000$ and vinyl group content of 0.07 %, at 140°C. The amount of platinum catalyst added assured platinum content in the elastomer equal to 50 ppm. Silica filled polymer phase is then cooled down to temperature 110°C, and 45 weight parts of quartz powder, 5 weight parts of wollastonite, 2 weight parts of titanium dioxide and 5 weight parts of the hybrid systems $MgO \cdot SiO_2$ /multiwalled oligomeric silsesquioxanes, containing 10 weight parts of silsesquioxane octa-substituted with methacrylo- groups on 100 weight parts of magnesium silicate filler, are admixed.

[0015] Prepared in this way silicone composite, subjected to curing with 1.5 weight % of bis(2,4-dichlorobenzoyl) peroxide during 15 minutes at 120 °C, exhibits the properties listed below:

	Results	Requirements of cable industry
Tensile strength [MPa]	7.7	min. 5.0
Elongation at break [%]	247	min. 150
Tear strength [kN/m]	16	min. 12
Hardness [°Sh A]	64	70±5
Time to ceramization of cured composite under the flame from gas burner at 1050 °C [s]	below 60	

Example no. 2

[0016] 40 weight parts of pyrogenic silica, having the specific surface area of 200 m²/g and platinum catalyst in the form of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane are admixed to 100 weight parts of dimethyl-vinyl silicone of average molecular weight $M_w = 680\,000$ and vinyl group content of 0.12 %, at 140°C. The amount of platinum catalyst added assured platinum content in the elastomer equal to 50 ppm. Silica filled polymer phase is then cooled down to temperature 80°C, and 35 weight parts of potassium mica, 10 weight parts of aluminum hydroxide, 3 weight parts of magnesium hydroxide, 2 weight parts of titanium dioxide and 8 weight parts of the hybrid systems $MgO \cdot SiO_2$ /multiwalled oligomeric silsesquioxanes, containing 20 weight parts of silsesquioxane octa-substituted with methacrylo- groups on 100 weight parts of magnesium silicate filler, are admixed.

[0017] Prepared in this way silicone composite, subjected to curing with 1.5 weight % of bis(2,4-dichlorobenzoyl)peroxide during 15 minutes at 120 °C, exhibits the properties listed below:

	Results	Requirements of cable industry
Tensile strength [MPa]	6.1	min. 5.0
Elongation at break [%]	207	min. 150
Tear strength [kN/m]	18	min. 12
Hardness [°Sh A]	73	70±5
Time to ceramization of cured composite under the flame from gas burner at 1050 °C [s]	below 60	

Claims

1. Application of the hybrid systems $MgO \cdot SiO_2$ /multiwalled oligomeric silsesquioxanes, in silicone composites containing magnesium silicate and from 0.1 to 50 weight parts of the silsesquioxanes, favourably 10 weight parts, containing $R_1 - R_8$, where R_1 to R_8 is alkyl- group and/or groups, or alkoxy-, or methacryloxy-, or glycidoxy-, or amino-, or vinyl-, or perfluoro- or their mixture, used for its modification, as promoters of ceramization in the silicone composites destined for covers of electrical cables.



EUROPEAN SEARCH REPORT

Application Number
EP 13 46 0078

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	DAMIAN AMBROZEWICZ ET AL: "New POSS/magnesium silicate nano-hybrids obtained by chemical or mechanical methods", CHEMICAL ENGINEERING JOURNAL, vol. 210, 30 August 2012 (2012-08-30), pages 229-236, XP055113413, ISSN: 1385-8947, DOI: 10.1016/j.cej.2012.08.075 * figure 5(b) * -----	1	INV. C04B35/00 C08J5/12 C08J5/18 C08G77/04 C08L83/04
			TECHNICAL FIELDS SEARCHED (IPC)
			C04B C08J C08G C08L
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 10 April 2014	Examiner Bergmeier, Martin
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 20090099289 A [0008]
- PL P394903 [0011]

Non-patent literature cited in the description

- **J.E. MARK.** Ceramic - modified elastomers. *Current Opinion in Solid State and Materials Science*, 1999, vol. 4, 565-570 [0007]