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(54) Title: SILICONE RESINS AND THEIR USE IN POLYMER COMPOSITIONS

(57) Abstract: Branched silicone (organopolysiloxane) resins and preparation method and use thereof are provided, which contain at least one group selected from phosphonate and phosphinate groups and at least one organic group containing nitrogen. Such silicone resins can be used in thermoplastic, thermosetting or rubber organic polymer compositions to reduce the flammability of the organic polymer compositions.

## SILICONE RESINS AND THEIR USE IN POLYMER COMPOSITIONS

5 [0001] This invention relates to branched silicone (organopolysiloxane) resins. It also relates to the preparation of such organopolysiloxanes and to their use in thermoplastic, thermosetting or rubber organic polymer compositions to reduce the flammability of the organic polymer compositions.

10 [0002] US-A- 2007/0167597 describes phosphone ester modified organosilicon compounds prepared by reacting phosphonic ester functionalized alkoxy silane with a silanol-functional organosilicon compound.

15 [0003] CN-A-101274998 describes an epoxy phosphorus-containing hybridization hardener with heat resistance and flame retardancy for electron polymer material and a preparation method thereof. The phosphorus-containing hybridization hardener is a nanometer-sized organic/inorganic hybrid silicone of a hollow enclosed type or a partially enclosed type, wherein the structure centre of the silicone consists of inorganic skeleton Si-O bonds. The external structure consists of organic groups of organic phosphor or amidogen or imidogen.

20 [0004] The paper 'Thermal Degradation Behaviours of Polypropylene with novel Silicon-containing Intumescent Flame Retardant' by Qiang Li et al in J. Applied Polymer Science, Vol. 98, 2487-2492 (2005) describes the synthesis of N-[3-(dimethoxy-methyl-silanyl)-propyl]-N'-(9-methyl-3,9-dioxo-2,4,8,10-tetraoxa-3,9-diphospha-spiro-[5.5]undec-3-yl)-ethane-1,2-diamine / dimethoxy dimethyl silane copolymer and its incorporation into  
25 polypropylene to enhance the flame retardancy of the polypropylene. The paper 'Preparation and properties of halogen-free flame retardant epoxy resins with phosphorus-containing siloxanes' by Jiapei Ding et al in Polymer Bulletin, Vol. 62, 829-841 (2009) describes epoxy resin modifiers synthesized by addition reaction of  
30 divinyltetramethyldisiloxane with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO).

35 [0005] The paper 'Synthesis, characterization and catalytic activity of porous vanadyl phosphonate-modified silicas' by M. Jurado-Gonzalez et al in J. Mater. Chem., Vol. 12, 3605-3609 (2002) describes synthetic routes to ethylphosphonic acid-modified silicas. The modified silicas are mesoporous solids with potential use as catalysts.

**[0006]** The paper 'Effect of Flame Retardant containing Phosphorus and Silicone on Thermal Performance of PC/ABS' by Wei Ping et al in Journal of Wuhan University of Technology – Mater. Sci. Ed. April 2009 at pp 235-240 describes a flame retardant  
5 comprising polydimethylsiloxane having a pendant group containing a DOPO moiety.

**[0007]** The paper 'Thermal degradation behaviours and flame retardancy of PC/ABS with novel silicon-containing flame retardant' by Hanfang Zhong et al. in Fire. Mater. Vol. 31, 411-423 (2007) describes a novel flame retardant containing silicon, phosphorus and nitrogen  
10 synthesised from the reaction of DOPO, vinylmethyldimethoxysilane and N- $\beta$ -(aminoethyl)- $\gamma$ -aminopropyl methyl dimethoxy silane.

**[0008]** The paper 'Siloxane-phosphonate finishes on cellulose: thermal characterization and flammability data' presented by S. Gallagher et al at 2004 Beltwide Cotton Conferences  
15 describes applying siloxane phosphonate monomers to cotton fabric.

**[0009]** The paper 'Polybenzoxazine containing polysilsesquioxane: preparation and thermal properties' by Yonghong Liu et al. in Journal of Applied Polymer Science (2006),  
20 99(3), 927-936 describes a benzoxazine-bearing trimethoxysilane and its hydrolysis and condensation to a polysilsesquioxane, which could be reacted with difunctional benzoxazine of bisphenol A to form inorganic-organic hybrids of improved thermal stability.

**[0010]** Due to the widespread and increasing use of synthetic polymers, there are a large number of flame retardant compounds in use in today's plastic markets. Halogen containing  
25 flame retardants have performed well in terms of flame retardancy properties, processability, cost, etc, however there is an urgent need for halogen-free flame retardants (HFFR) as polymer additives, which comply with environmental regulations, OEM perception, customers requirements, etc. Fire safety is now based on preventing ignition and reducing flame spread through reducing the rate of heat release, as well as on reducing fire toxicity.  
30 Flame retardant additives must be safe in what concerns health and environment, must be cost efficient and maintain/improve plastics performance.

**[0011]** The halogenated flame retardant compounds act mostly in the vapour phase by a radical mechanism to interrupt the exothermic processes and to suppress combustion.

Examples are the bromine compounds, such as tetrabromobisphenol A, chlorine compounds, halogenated phosphate ester, etc.

**[0012]** Among the halogen-free flame retardants one can find the metal hydroxides, such as magnesium hydroxide ( $Mg(OH)_2$ ) or aluminium hydroxide ( $Al(OH)_3$ ), which act by heat absorbance, i.e. endothermic decomposition into the respective oxides and water when heated, however they present low flame retardancy efficiency, low thermal stability and significant deterioration of the physical/chemical properties of the matrices. Other compounds act mostly on the condensed phase, such as expandable graphite, organic phosphorous (e.g. phosphate, phosphonates, phosphine, phosphine oxide, phosphonium compounds, phosphites, etc.), ammonium polyphosphate, etc. Zinc borate, nanoclays and red phosphorous are other examples of halogen-free flame retardants. Silicon-containing additives are known to significantly improve the flame retardancy, acting both through char formation in the condensed phase and by the trapping of active radicals in the vapour phase. Sulfur-containing additives, such as potassium diphenylsulfone sulfonate (KSS), are well known flame retardant additives for thermoplastics, in particular for polycarbonate.

**[0013]** Either the halogenated, or the halogen-free compounds can act by themselves, or as synergetic agent together with the compositions claimed in the present patent to render the desired flame retardance performance to many polymer matrices. For instance, phosphonate and phosphine or phosphine oxide have been referred in the literature as being anti-dripping agents and can be used in synergy with the flame retardant additives disclosed in the present patent. The paper "Flame-retardant and anti-dripping effects of a novel char-forming flame retardant for the treatment of poly(ethylene terephthalate) fabrics" presented by Dai Qi Chen et al. at 2005 Polymer Degradation and Stability describes the application of a phosphonate, namely poly(2-hydroxy propylene spirocyclic pentaerythritol bisphosphonate) to impart flame retardance and dripping resistance to poly(ethylene terephthalate) (PET) fabrics. Benzoguanamine has been applied to PET fabrics to reach anti-dripping performance as reported by Hong-yan Tang et al. at 2010 in "A novel process for preparing anti-dripping polyethylene terephthalate fibres", Materials & Design. The paper "Novel Flame-Retardant and Anti-dripping Branched Polyesters Prepared via Phosphorus-Containing Ionic Monomer as End-Capping Agent" by Jun-Sheng Wang et al. at 2010 reports on a series of novel branched polyester-based ionomers which were synthesized with trihydroxy ethyl esters of trimethyl-1,3,5-benzentricarboxylate (as branching agent) and sodium salt of 2-hydroxyethyl 3-(phenylphosphinyl)propionate (as end-capping agent) by

melt polycondensation. These flame retardant additives dedicated to anti-dripping performance can be used in synergy with the flame retardant additives disclosed in this patent. Additionally, the flame retardant additives disclosed in this patent have demonstrated synergy with other well-known halogen-free additives, such as KSS, Zinc Borates and Metal Hydroxydes (aluminium trihydroxyde or Magnesium dihydroxyde). When used as synergists, classical flame retardants such as KSS, Zinc Borates or Metal Hydroxydes (aluminium trihydroxyde or magnesium dihydroxyde) can be either physically blended or surface pre-treated with the silicon based additives disclosed in this patent prior to compounding.

10 **[0014]** A branched silicone resin according to the present invention contains at least one group selected from phosphonate and phosphinate groups and at least one organic group containing nitrogen.

**[0015]** The invention includes the use of such a branched silicone resin in a thermoplastic, thermosetting or rubber organic polymer composition to reduce the flammability of the organic polymer composition, and includes a thermoplastic, thermoset or rubber organic polymer composition comprising a thermoplastic, thermoset or rubber organic polymer and a branched silicone resin as defined above. The invention also includes the use of such a branched silicone resin as a fire resistant coating on a substrate.

20 **[0016]** The invention also includes a thermoplastic, thermoset or rubber organic polymer composition comprising a thermoplastic, thermoset or rubber organic polymer, a branched silicone resin containing at least one group selected from phosphonate and phosphinate groups and a branched silicone resin containing at least one organic group containing nitrogen.

**[0017]** Polyorganosiloxanes, also known as silicones, generally comprise siloxane units selected from  $R_3SiO_{1/2}$  (M units),  $R_2SiO_{2/2}$  (D units),  $RSiO_{3/2}$  (T units) and  $SiO_{4/2}$  (Q units), in which each R represents an organic group or hydrogen or a hydroxyl group. Branched silicone resins contain T and/or Q units, optionally in combination with M and/or D units. In the branched silicone resins of the invention, at least 25% of the siloxane units are preferably T and/or Q units. More preferably, at least 75% of the siloxane units in the branched silicone resin are T and/or Q units.

**[0018]** In a process for the preparation of a branched silicone resin according to the invention, at least one alkoxy silane of the formula  $R_P Si(OR')_3$ ,  $R_P R^{11} Si(OR')_2$  or  $R_P R^{11}_2 SiOR'$ , at least one alkoxy silane of the formula  $R_N Si(OR')_3$ ,  $R_N R^{12} Si(OR')_2$  or  $R_P R^{12}_2 SiOR'$ , and optionally one or more alkoxy silane of the formula  $Si(OR')_4$ ,  $R^4 Si(OR')_3$ ,  $R^4_2 Si(OR')_2$  or  $R^4_3 SiOR'$ , where each  $R'$ , which can be the same or different, is an alkyl group having 1 to 4 carbon atoms; each  $R_P$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent; each  $R^{11}$  which can be the same or different is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent; each  $R_N$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing an organic nitrogen substituent; each  $R^{12}$  which can be the same or different is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing an organic nitrogen substituent; and each  $R^4$  which can be the same or different is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms, are hydrolysed and condensed to form siloxane bonds.

**[0019]** In an alternative process for the preparation of a branched silicone resin according to the invention, at least one alkoxy silane of the formula  $R_P R_N Si(OR')_2$  or  $R_P R_N R^{13} SiOR'$ , and optionally one or more alkoxy silane of the formula  $Si(OR')_4$ ,  $R^4 Si(OR')_3$ ,  $R^4_2 Si(OR')_2$ ,  $R^4_3 SiOR'$ ,  $R_P Si(OR')_3$ ,  $R_P R^{11} Si(OR')_2$ ,  $R_P R^{11}_2 SiOR'$ ,  $R_N Si(OR')_3$ ,  $R_N R^{12} Si(OR')_2$  or  $R_P R^{12}_2 SiOR'$ , where each  $R'$  which can be the same or different is an alkyl group having 1 to 4 carbon atoms; each  $R_P$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent; each  $R_N$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing an organic nitrogen substituent; each  $R^{13}$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent or an organic nitrogen substituent; each  $R^4$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms; each  $R^{11}$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent; and each  $R^{12}$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms or an alkyl, cycloalkyl,

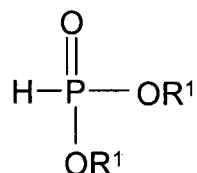
alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing an organic nitrogen substituent, is hydrolysed and condensed to form siloxane bonds.

**[0020]** In a further alternative process for the preparation of a branched silicone resin according to the invention, at least one alkoxy silane of the formula  $R_b\text{Si}(\text{OR}')_3$ ,  $R_b\text{R}^{13}\text{Si}(\text{OR}')_2$  or  $R_b\text{R}^{13}_2\text{SiOR}'$ , and optionally one or more alkoxy silane of the formula  $\text{Si}(\text{OR}')_4$ ,  $\text{R}^4\text{Si}(\text{OR}')_3$ ,  $\text{R}^4_2\text{Si}(\text{OR}')_2$ ,  $\text{R}^4_3\text{SiOR}'$ ,  $\text{R}_p\text{Si}(\text{OR}')_3$ ,  $\text{R}_p\text{R}^{11}\text{Si}(\text{OR}')_2$ ,  $\text{R}_p\text{R}^{11}_2\text{SiOR}'$ ,  $\text{R}_n\text{Si}(\text{OR}')_3$ ,  $\text{R}_n\text{R}^{12}\text{Si}(\text{OR}')_2$  or  $\text{R}_p\text{R}^{12}_2\text{SiOR}'$ , where each  $\text{R}'$  which can be the same or different is an alkyl group having 1 to 4 carbon atoms, each  $\text{R}_b$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing both a phosphonate or phosphinate substituent and an organic nitrogen group; each  $\text{R}^{13}$  which can be the same or different is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent and/or an organic nitrogen group;  $\text{R}_p$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent;  $\text{R}_n$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing an organic nitrogen substituent; each  $\text{R}^4$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms, each  $\text{R}^{11}$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent; and each  $\text{R}^{12}$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing an organic nitrogen substituent, is hydrolysed and condensed to form siloxane bonds.

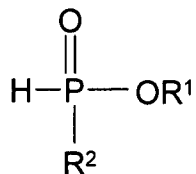
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**[0021]** In a process according to another aspect of the invention for the preparation of an organopolysiloxane containing a phosphonate or phosphinate group, characterized in that an organopolysiloxane containing an olefinically unsaturated group is reacted with a phosphite of the formula

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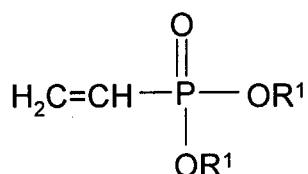


or a phosphinate of the formula

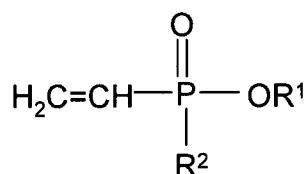


5 where each R<sup>1</sup> which can be the same or different is an alkyl group having 1 to 12 carbon atoms, and R<sup>2</sup> is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms, in the presence of a free radical initiator.

10 **[0022]** In a process according to another aspect of the invention for the preparation of an organopolysiloxane containing a phosphonate or phosphinate group, characterized in that an organopolysiloxane containing an amino group is reacted with an olefinic phosphite of the formula



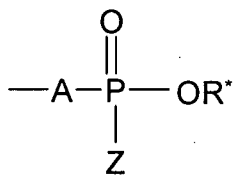
15 or an olefinic phosphinate of the formula



20 where each R<sup>1</sup> which can be the same or different is an alkyl group having 1 to 12 carbon atoms, and R<sup>2</sup> is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms.

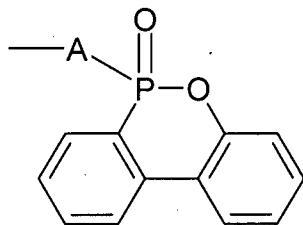
25 **[0023]** The branched silicone resin of the invention preferably contains at least one phosphonate or phosphinate moiety present in a T unit of the formula R<sub>P</sub>SiO<sub>3/2</sub>, where R<sub>P</sub> is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent. The group R<sub>P</sub> can for example have the formula





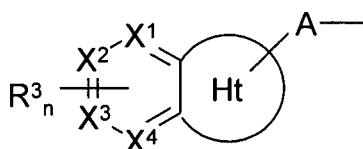
where A is a divalent hydrocarbon group having 1 to 20 carbon atoms and R\* is an alkyl or aryl group having 1 to 12 carbon atoms. If the group R<sub>P</sub> contains a phosphonate substituent, Z is preferably a group of the formula —OR\*. If the group R<sub>P</sub> contains a phosphinate substituent, Z is preferably an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms. Preferred groups R<sub>P</sub> include 2-(diethylphosphonato)ethyl, 3-(diethylphosphonato)propyl, 2-(dimethylphosphonato)ethyl, 3-(dimethylphosphonato)propyl, 2-(ethyl(ethylphosphinato))ethyl and 3-(ethyl(ethylphosphinato))propyl.

**[0024]** The phosphinate substituent can alternatively comprise a 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide group, sometimes known as a DOPO group. The group R<sub>P</sub> can for example have the formula



where A is a divalent hydrocarbon group having 1 to 20 carbon atoms, for example 2-DOPO-ethyl or 3-DOPO-propyl.

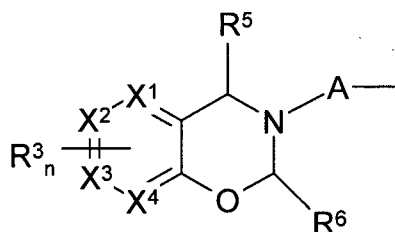
**[0025]** The branched silicone resin of the invention preferably contains at least one organic nitrogen-containing group present in a T unit of the formula R<sub>N</sub>SiO<sub>3/2</sub>, where R<sub>N</sub> is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a organic nitrogen substituent. In one preferred type of resin according to the invention the organic group containing nitrogen is a heterocyclic group present as a group of the formula



where  $X^1$ ,  $X^2$ ,  $X^3$  and  $X^4$  independently represent a CH group or a N atom and form a benzene, pyridine, pyridazine, pyrazine, pyrimidine or triazine aromatic ring; Ht represents a heterocyclic ring fused to the aromatic ring and comprising 2 to 8 carbon atoms, 1 to 4 nitrogen atoms and optionally 1 or 2 oxygen and/or sulphur atoms; A represents a divalent organic linkage having 1 to 20 carbon atoms bonded to a nitrogen atom of the heterocyclic ring; the heterocyclic ring can optionally have one or more substituent groups selected from alkyl, substituted alkyl, cycloalkyl, alkenyl, alkynyl, aryl and substituted aryl groups having 1 to 12 carbon atoms and amino, nitrile, amido and imido groups; and  $R^3_n$ , with  $n = 0 - 4$ , represents an alkyl, substituted alkyl, alkenyl group having 1 to 8 carbon atoms or cycloalkyl, alkynyl, aryl or substituted aryl group having 1 to 40 carbon atoms, or an amino, nitrile, amido or imido group or a carboxylate  $-C(=O)-O-R^4$ , oxycarbonyl  $-O-(C=O)-R^4$ , carbonyl  $-C(=O)-R^4$ , or an oxy  $-O-R^4$  substituted group with  $R^4$  representing hydrogen or an alkyl, cycloalkyl, alkenyl, alkynyl, aryl, or substituted aryl groups having 1 to 40 carbon atoms, substituted on one or more positions of the aromatic ring, or two groups  $R^3$  can be joined to form a ring system comprising at least one carbocyclic or heterocyclic ring fused to the aromatic ring.

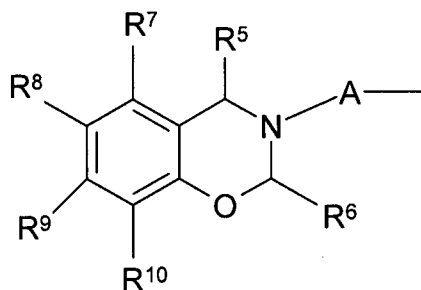
**[0026]** The heterocyclic ring Ht is preferably not a fully aromatic ring, i.e. it is preferably not a pyridine, pyridazine, pyrazine, pyrimidine or triazine aromatic ring. The heterocyclic ring Ht can for example be an oxazine, pyrrole, pyrroline, imidazole, imidazoline, thiazole, thiazoline, oxazole, oxazoline, isoxazole or pyrazole ring. Examples of preferred heterocyclic ring systems include benzoxazine, indole, benzimidazole, benzothiazole and benzoxazole. In some preferred resins the heterocyclic ring is an oxazine ring so that  $R_N$  is a group of the formula

25



where  $X^1$ ,  $X^2$ ,  $X^3$  and  $X^4$ , A,  $R^3$  and  $n$  are defined as above and  $R^5$  and  $R^6$  each represent hydrogen, an alkyl, substituted alkyl, cycloalkyl, alkenyl, alkynyl, aryl or substituted aryl group having 1 to 12 carbon atoms, or an amino or nitrile group. The group can for example be a benzoxazine group of the formula

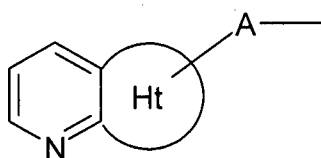
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5 where  $R^7$ ,  $R^8$ ,  $R^9$  and  $R^{10}$  each represent hydrogen, an alkyl, substituted alkyl, alkenyl group having 1 to 8 carbon atoms or cycloalkyl, alkynyl, aryl or substituted aryl group having 1 to 40 carbon atoms, or an amino, nitrile, amido or imido group or a carboxylate  $-C(=O)-O-R^4$ , oxycarbonyl  $-O-(C=O)-R^4$ , carbonyl  $-C(=O)-R^4$ , or an oxy  $-O-R^4$  substituted group with  $R^4$  representing hydrogen or an alkyl, cycloalkyl, alkenyl, alkynyl, aryl, or substituted aryl groups having 1 to 40 carbon atoms, or  $R^7$  and  $R^8$ ,  $R^8$  and  $R^9$  or  $R^9$  and  $R^{10}$  can each be joined to form a ring system comprising at least one carbocyclic or heterocyclic ring fused to the benzene ring.

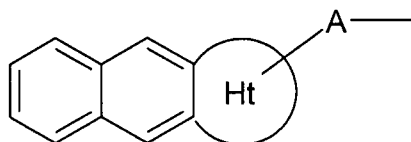
10 [0027] The oxazine or other heterocyclic ring Ht can alternatively be bonded to a pyridine ring to form a heterocyclic group of the formula

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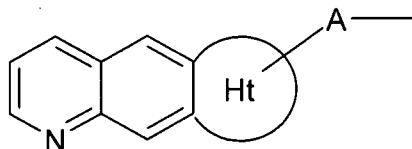


20 [0028] The benzene, pyridine, pyridazine, pyrazine or triazine aromatic ring can be annelated to a ring system comprising at least one carbocyclic or heterocyclic ring to form an extended ring system enlarging the pi-electron conjugation. A benzene ring can for example be annelated to another benzene ring to form a ring system containing a naphthanene moiety

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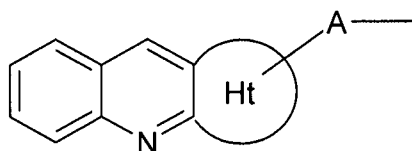


such as a naphthoxazine group, or can be annelated to a pyridine ring to form a ring system containing a quinoline moiety.



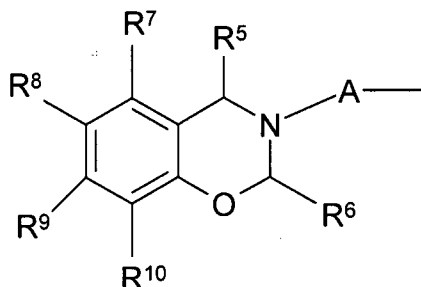
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**[0029]** A pyridine ring can for example be annelated to a benzene ring to form a ring system containing a quinoline moiety in which the heterocyclic ring Ht, for example an oxazine ring, is fused to the pyridine ring



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**[0030]** The aromatic ring can be annelated to a quinone ring to form a naphthoquinoid or anthraquinoid structure. In an alkoxy silane of the formula



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the groups  $R^8$  and  $R^9$ ,  $R^7$  and  $R^8$ , or  $R^9$  and  $R^{10}$  can form an annelated ring of naphthoquinoid or anthraquinoid structure. Such ring systems containing carbonyl groups may form resins having improved solubility in organic solvents, allowing easier application to polymer compositions.

20

**[0031]** The organic group  $R_N$  containing nitrogen can alternatively comprise an aminoalkyl or aminoaryl group containing 1 to 20 carbon atoms and 1 to 3 nitrogen atoms bonded to a silicon atom of the silicone resin, for example  $-(CH_2)_3NH_2$ ,  $-(CH_2)_4NH_2$ , -

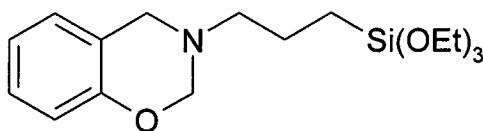
$(CH_2)_3NH(CH_2)_2NH_2$ ,  $-CH_2CH(CH_3)CH_2NH_2$ ,  $-CH_2CH(CH_3)CH_2NH(CH_2)_2NH_2$ , -

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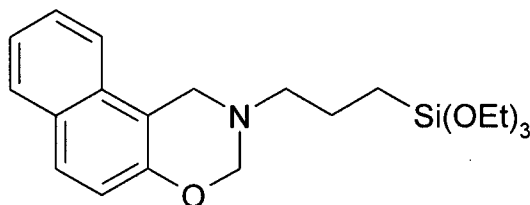
(CH<sub>2</sub>)<sub>3</sub>NHCH<sub>2</sub>CH<sub>2</sub>NH(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>, -CH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>NH(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>, -  
 (CH<sub>2</sub>)<sub>3</sub>NH(CH<sub>2</sub>)<sub>4</sub>NH<sub>2</sub> or -(CH<sub>2</sub>)<sub>3</sub>O(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>, or -(CH<sub>2</sub>)<sub>3</sub>NHC<sub>6</sub>H<sub>4</sub>, -(CH<sub>2</sub>)<sub>3</sub>NH(CH<sub>2</sub>)<sub>2</sub>NHC<sub>6</sub>H<sub>4</sub>,  
 -(CH<sub>2</sub>)<sub>3</sub>NHCH<sub>3</sub>, -(CH<sub>2</sub>)<sub>3</sub>N(C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>.

- 5 **[0032]** A branched silicone resin of the invention containing at least one phosphonate or phosphinate moiety present in a T unit of the formula R<sub>P</sub>SiO<sub>3/2</sub> can for example be prepared by a process in which a trialkoxysilane of the formula R<sub>P</sub>Si(OR')<sub>3</sub> is hydrolysed and condensed to form siloxane bonds. Examples of useful trialkoxysilanes containing a R<sub>P</sub> group are 2-(diethylphosphonato)ethyltriethoxysilane, 3-  
 10 (diethylphosphonato)propyltriethoxysilane and 2-(DOPO)ethyltriethoxysilane.

- [0033]** A branched silicone resin of the invention containing at least one organic nitrogen-containing group present in a T unit of the formula R<sub>N</sub>SiO<sub>3/2</sub> can for example be prepared by a process in which a trialkoxysilane of the formula R<sub>N</sub>Si(OR')<sub>3</sub> is hydrolysed and condensed to form siloxane bonds. Examples of useful trialkoxysilanes containing a R<sub>N</sub> group are 3-(3-  
 15 benzoxazinyl)propyltriethoxysilane

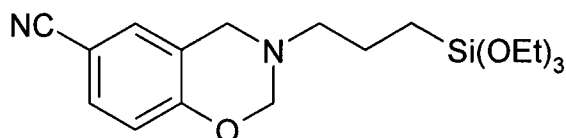


- 20 and the corresponding naphthoxazinetriethoxysilane,

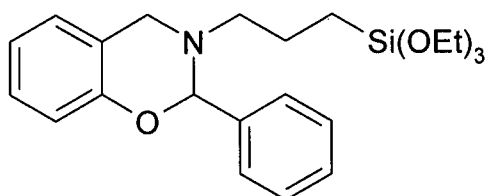


3-(6-cyanobenzoxazinyl-3)propyltriethoxysilane,

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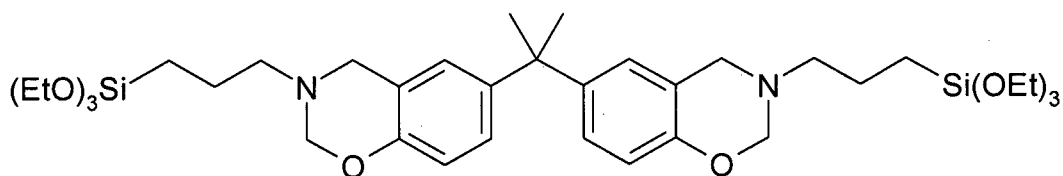


3-(2-phenylbenzoxazinyl-3)propyltriethoxysilane



5 and 3-aminopropyltrimethoxysilane.

**[0034]** The branched silicone resin containing at least one organic nitrogen-containing group can be formed from a bis(alkoxysilane), for example a bis(trialkoxysilane), containing two heterocyclic rings each having an alkoxysilane substituent, such as 1,3-bis(3-(3-  
10 trimethoxysilylpropyl)benzoxazinyl-6)-2,2-dimethylpropane



**[0035]** The branched silicone resin can in one preferred embodiment comprises mainly T  
15 units, that is at least 50 mole % T units, and more preferably at least 80 or 90% T units. It can for example comprise substantially all T units. The trialkoxysilanes of the formulae  $R_P Si(OR')_3$  and  $R_N Si(OR')_3$  can be co-hydrolysed and condensed, optionally with an alkoxysilane of the formula  $R^4 Si(OR')_3$ , in which each  $R'$  is an alkyl group having 1 to 4 carbon atoms and  $R^4$  represents an alkyl, cycloalkyl, aminoalkyl, alkenyl, alkynyl, aryl or  
20 aminoaryl group having 1 to 20 carbon atoms. Examples of useful trialkoxysilanes of the formula  $R^4 Si(OR')_3$  are alkyltrialkoxysilanes such as methyltriethoxysilane, ethyltriethoxysilane, methyltrimethoxysilane, aryltrialkoxysilanes such as phenyltriethoxysilane and alkenyltrialkoxysilanes such as vinyltrimethoxysilane.

**[0036]** Alternative alkoxysilanes containing a phosphonate or phosphinate group  
25 are monoalkoxysilanes for example of the formula  $R_P R^{11}_2 SiOR'$  and dialkoxysilanes for example of the formula  $R_P R^{11} Si(OR')_2$ , where each  $R'$  is an alkyl group having 1 to 4 carbon atoms; each  $R_P$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent; and each  $R^{11}$  which can be the

same or different is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent. Examples of suitable monoalkoxysilanes containing a phosphonate or phosphinate group are 2-

- 5 (DOPO)ethyldimethylethoxysilane and 3-(diethylphosphonato)propyldimethylethoxysilane. Examples of suitable dialkoxysilanes containing a phosphonate or phosphinate group are 2-(DOPO)ethylmethyldiethoxysilane and 3-(diethylphosphonato)propylmethyldiethoxysilane.

**[0037]** Alternative alkoxysilanes containing an organic nitrogen-containing group are  
10 monoalkoxysilanes for example of the formula  $R_N R^{12}_2 SiOR'$  and dialkoxysilanes for example of the formula  $R_N R^{12}_2 Si(OR')_2$  where each  $R_N$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing an organic nitrogen substituent; and each  $R^{12}$  which can be the same or different is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group  
15 having 1 to 20 carbon atoms containing an organic nitrogen substituent. Examples of suitable monoalkoxysilanes containing an organic nitrogen substituent are 3-(3-benzoxaziny)propyldimethylethoxysilane and 3-aminopropyldimethylethoxysilane. Examples of suitable dialkoxysilanes containing an organic nitrogen substituent are 3-(3-benzoxaziny)propylmethyldiethoxysilane and 3-aminopropylmethyldimethoxysilane.

20

**[0038]** Monoalkoxysilanes when hydrolysed and condensed will form M groups in the silicone resin and dialkoxysilanes when hydrolysed and condensed will form D groups in the silicone resin. A monoalkoxysilane or dialkoxysilane containing a  $R_P$  group can be reacted with trialkoxysilanes and/or tetraalkoxysilanes to form a branched silicone resin. A  
25 monoalkoxysilane or dialkoxysilane containing a  $R_P$  group can be reacted with a trialkoxysilane containing a  $R_N$  group, and optionally another trialkoxysilane and/or a tetraalkoxysilane, to form a branched silicone resin according to the invention. A monoalkoxysilane or dialkoxysilane containing a  $R_N$  group can be reacted with a trialkoxysilane containing a  $R_P$  group, and optionally another trialkoxysilane and/or a  
30 tetraalkoxysilane, to form a branched silicone resin according to the invention. Alternatively a monoalkoxysilane or dialkoxysilane containing a  $R_P$  group can be reacted with a monoalkoxysilane or dialkoxysilane containing a  $R_N$  group and a trialkoxysilane and/or a tetraalkoxysilane to form a branched silicone resin according to the invention. For example a monoalkoxysilane containing a  $R_P$  group and a monoalkoxysilane containing a  $R_N$  group  
35 can be reacted with tetraethoxysilane to form a MQ branched silicone resin.

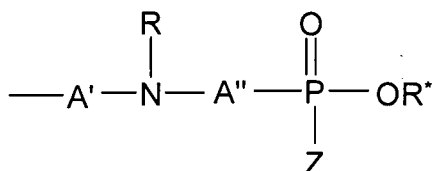
**[0039]** The branched silicone resin of the invention can alternatively be formed from an alkoxy silane containing both a phosphonate or phosphinate group and an organic nitrogen-containing group. Examples of such alkoxy silanes include dialkoxy silanes of the formula  $R_P R_N Si(OR')_2$  and monoalkoxy silanes of the formula  $R_P R_N R^{13} SiOR'$ , where each  $R'$  is an alkyl group having 1 to 4 carbon atoms; each  $R_P$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent; each  $R_N$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing an organic nitrogen substituent; and each  $R^{13}$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent or an organic nitrogen substituent. Examples of dialkoxy silanes include 2-DOPO-ethyl 3-aminopropyl dimethoxy silane and 3-(diethylphosphonato)propyl 3-(3-benzoxazinyl)propyl dimethoxy silane. Examples of monoalkoxy silanes include 2-DOPO-ethyl 3-aminopropyl methyl methoxy silane and 3-(diethylphosphonato)propyl 3-(3-benzoxazinyl)propyl methyl methoxy silane. Such alkoxy silanes can be hydrolysed and condensed with at least one alkoxy silane of the formula  $Si(OR')_4$ ,  $R^4 Si(OR')_3$ ,  $R_P Si(OR')_3$  or  $R_N Si(OR')_3$ , and optionally one or more alkoxy silane of the formula  $R^4_2 Si(OR')_2$ ,  $R^4_3 SiOR'$ ,  $R_P R^{11} Si(OR')_2$ ,  $R_P R^{11}_2 SiOR'$ ,  $R_N R^{12} Si(OR')_2$  or  $R_P R^{12}_2 SiOR'$ , where each  $R^4$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms; each  $R^{11}$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent; and each  $R^{12}$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing an organic nitrogen substituent, to form a branched silicone resin according to the invention.

**[0040]** An alternative example of an alkoxy silane containing both a phosphonate or phosphinate group and an organic nitrogen-containing group is an alkoxy silane in which the phosphonate or phosphinate group and the organic group containing nitrogen are both present in a single group bonded to the silicon atom of the alkoxy silane. Examples of such alkoxy silanes have the formula  $R_b Si(OR')_3$ ,  $R_b R^{13} Si(OR')_2$  or  $R_b R^{13}_2 SiOR'$ , where each  $R'$  is an alkyl group having 1 to 4 carbon atoms, each  $R_b$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing both a phosphonate or phosphinate substituent and an organic nitrogen group; each  $R^{13}$  is an alkyl, cycloalkyl, alkenyl, alkynyl or

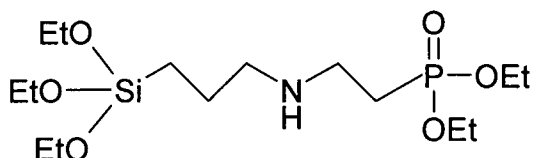


aryl group having 1 to 20 carbon atoms or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent and/or an organic nitrogen group. Such an alkoxy silane can be hydrolysed and condensed to form siloxane bonds, optionally together with one or more alkoxy silane of the formula  $\text{Si}(\text{OR}')_4$ ,  $\text{R}^4\text{Si}(\text{OR}')_3$ ,  $\text{R}^4_2\text{Si}(\text{OR}')_2$ ,  $\text{R}^4_3\text{SiOR}'$ ,  $\text{R}_\text{P}\text{Si}(\text{OR}')_3$ ,  $\text{R}_\text{P}\text{R}^{11}\text{Si}(\text{OR}')_2$ ,  $\text{R}_\text{P}\text{R}^{11}_2\text{SiOR}'$ ,  $\text{R}_\text{N}\text{Si}(\text{OR}')_3$ ,  $\text{R}_\text{N}\text{R}^{12}\text{Si}(\text{OR}')_2$  or  $\text{R}_\text{P}\text{R}^{12}_2\text{SiOR}'$ , where  $\text{R}_\text{P}$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent;  $\text{R}_\text{N}$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing an organic nitrogen substituent; each  $\text{R}^4$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms, each  $\text{R}^{11}$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent; and each  $\text{R}^{12}$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing an organic nitrogen substituent.

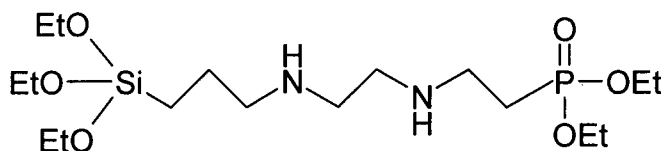
**[0041]** Examples of groups of the formula Rb are groups of the formula



where  $\text{A}'$  is a divalent organic group having 1 to 20 carbon atoms,  $\text{A}''$  is a divalent organic group having 1 to 20 carbon atoms,  $\text{R}^*$  is an alkyl group having 1 to 12 carbon atoms and  $\text{Z}$  is a group of the formula  $\text{---OR}^*$  or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 12 carbon atoms, or  $\text{R}^*$  and  $\text{Z}$  can be joined to form a heterocyclic ring, and  $\text{R}$  is hydrogen or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 12 carbon atoms, or can be joined to  $\text{A}''$  to form a heterocyclic ring. Examples of alkoxy silanes containing a group Rb are 3-(2-diethylphosphonatoethylamino)propyl triethoxysilane,



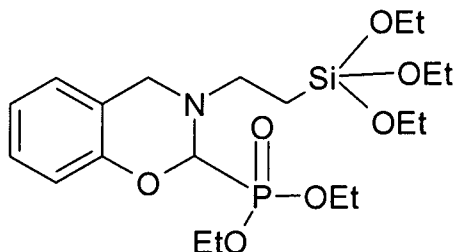
3-(2-dimethylphosphonatoethylamino)propyl trimethoxysilane, 3-(2-dimethylphosphonatoethylamino)propyl triethoxysilane, 3-(2-(2-phosphonatoethylamino)ethylamino)propyl triethoxysilane



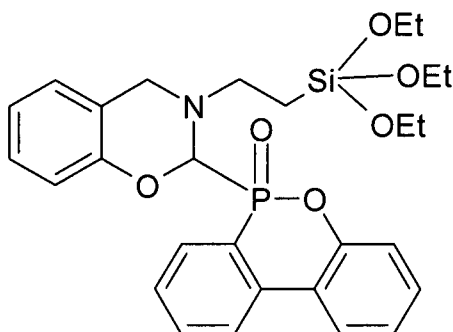
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and 3-(2-DOPO-ethylamino)propyl triethoxysilane. The alkoxy silane containing a group Rb can alternatively be an alkoxy silane-substituted nitrogen-containing heterocyclic compound, such as a benzoxazine alkoxy silane having a phosphonate substituent

10



or a DOPO substituent



15

**[0042]** The ratio of phosphonate or phosphinate groups to organic nitrogen-containing groups in the branched silicone resin can vary within a wide range. The molar ratio of phosphorus to nitrogen in the branched silicone resin can for example be in the range 1:9 to 9:1.

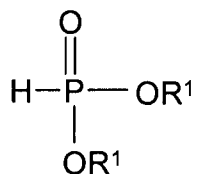
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[0043] The alkoxysilane containing a phosphonate or phosphinate group and the alkoxysilane containing an organic nitrogen-containing group (or the alkoxysilane containing both a phosphonate or phosphinate group and an organic nitrogen-containing group) can be hydrolysed and condensed alone but are more usually co-hydrolysed and condensed with another alkoxysilane, for example an alkyltrialkoxysilane or a tetraalkoxysilane. The alkoxysilane containing a phosphonate or phosphinate group and the alkoxysilane containing an organic nitrogen-containing group can for example be present at 10 to 100 mole% of the alkoxysilanes used to form the silicone resin, so that 10 to 100 mole% of the siloxane units in the silicone resin contain a phosphonate or phosphinate and/or an organic nitrogen-containing moiety.

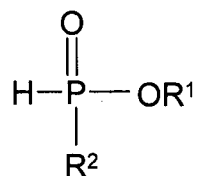
[0044] The branched silicone resin can be produced by heating the appropriate alkoxysilanes as described above in the presence of moisture or hydroxyl groups to cause hydrolysis and siloxane condensation of the alkoxysilane or alkoxysilanes. Atmospheric moisture may be sufficient to cause hydrolysis of the alkoxysilane(s), or water can be added in an amount up to an approximately stoichiometric amount with respect to the Si-bonded alkoxy groups, for example 0.5 to 1.5 moles water per alkoxy group. The reaction can be carried out in the absence of solvent or in a polar organic solvent such as a ketone, for example diethyl ketone or methyl isobutyl ketone. The reaction is preferably carried out at a temperature of 50-120°C. A siloxane condensation catalyst, for example an acid, base or organic tin compound, can be present but the reaction proceeds in the absence of catalyst.

[0045] If substantially all the alkoxysilanes reacted to form the branched silicone resin are trialkoxysilanes, the T-resins produced generally have a cage structure, usually a mixture of open and closed cage structures.

[0046] In an alternative process according to the invention, a branched silicone resin or other organopolysiloxane containing a phosphonate or phosphinate group is prepared by reacting an organopolysiloxane containing an olefinically unsaturated group is reacted with a phosphite of the formula



or a phosphinate of the formula



5 where each R<sup>1</sup> which can be the same or different is an alkyl or aryl group having 1 to 12 carbon atoms, and R<sup>2</sup> is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms, in the presence of a free radical initiator. Examples of suitable phosphites are diethyl phosphite and dimethyl phosphite. Examples of suitable phosphinates are DOPO (9, 10-Dihydro-9-Oxa-10-Phosphaphenanthrene-10-Oxide) and ethyl ethylphosphinate.

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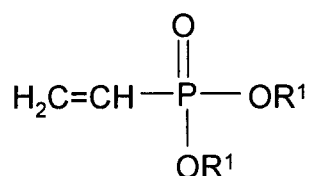
**[0047]** An example of a suitable branched silicone resin containing an olefinically unsaturated group is a resin containing a vinyl, allyl or hexenyl group, for example a vinyl T-resin formed by hydrolysis and condensation of a vinyltrialkoxysilane. Examples of other organopolysiloxanes containing an olefinically unsaturated group which can be reacted with the phosphite or phosphinate are polydiorganosiloxanes containing a vinyl, allyl or hexenyl group, for example polydimethylsiloxane (PDMS) containing unsaturated terminal groups such as dimethylvinylsilyl groups.

15

**[0048]** The free radical initiator can for example be an azo compound such as azobisisobutyronitrile (AIBN) or dimethylazodiisobutyrate, or can be a peroxide such as dicumyl peroxide or 2,5-dimethyl-2,5-di-(tert-butylperoxy)hexane. The organopolysiloxane containing an olefinically unsaturated group is preferably reacted with the phosphite in the presence of the free radical initiator at a temperature in the range 50 to 130°C.

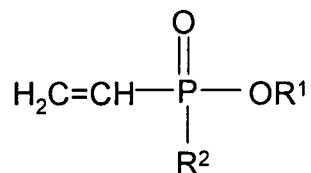
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25 **[0049]** In a further alternative process according to the invention, a branched silicone resin or other organopolysiloxane containing a phosphonate or phosphinate group is prepared by reacting an organopolysiloxane containing a primary or secondary amino group is reacted with an olefinic phosphite of the formula



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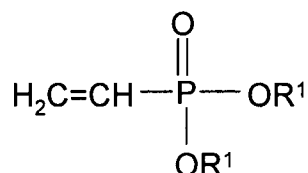
or an olefinic phosphinate of the formula



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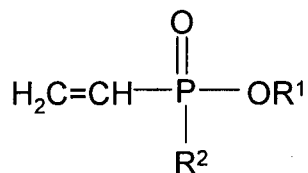
where each  $\text{R}^1$  which can be the same or different is an alkyl or aryl group having 1 to 12 carbon atoms, and  $\text{R}^2$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms. Examples of suitable vinyl phosphites are vinyl diethyl phosphite and vinyl dimethyl phosphite. Examples of suitable phosphinates are vinyl ethyl phosphinate. The organopolysiloxane containing a primary or secondary amino group can for example be a branched silicone resin containing an amino group. A silicone resin containing an amino group of the formula  $-\text{A}'-\text{NHR}$ , where  $\text{A}'$  and  $\text{R}$  are defined as above, can be reacted with an olefinic phosphite of the formula

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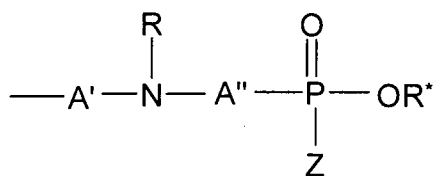
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or an olefinic phosphinate of the formula



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to form a silicone resin containing a group  $\text{Rb}$  of the formula



where A', R, Z and R\* are defined as above and A" is a  $-\text{CH}_2\text{CH}_2-$  or  $-\text{CH}(\text{CH}_3)-$  linkage.

**[0050]** The branched silicone resins of the invention have a high thermal stability which is higher than that of their non-phosphorylated counterparts and higher than that of linear  
5 silicone polymers. This higher thermal stability is due to the presence of the phosphorus atom that leads to the formation of highly stable polyphosphorylated silica ceramic structures. The flame retardancy imparted by the phosphorylated branched silicone resins is further increased by the presence of an organic nitrogen-containing group in the phosphorylated branched silicone resin. Such phosphorylated branched silicone resins additionally  
10 containing an amino group undergo an intumescent effect on intense heating, forming a flame resistant insulating char. An organic nitrogen-containing group is a nitrogen containing group linked to an organic moiety.

**[0051]** The branched silicone resins of the invention can be blended with a wide range of  
15 thermoplastic resins, for example polycarbonates, ABS (acrylonitrile butadiene styrene) resins, polycarbonate/ABS blends, polyesters, polystyrene, or polyolefins such as polypropylene or polyethylene. The branched silicone resins of the invention can also be blended with thermosetting resins, for example epoxy resins of the type used in electronics applications, which are subsequently thermoset, or unsaturated polyester resin. The  
20 branched silicone resins of the invention can also be blended with rubbers such as natural or synthetic rubbers. The mixtures of thermoplastics, thermosets or rubber with the branched silicone resins of the invention as additives have been proved to have a higher thermal stability, as shown by thermogravimetric (TGA) analysis, and better flame retardancy properties, as shown by TGA and the UL-94 test, and/or other flammability tests such as the  
25 glow wire test or cone calorimetry, compared to their non phosphorylated counterparts. The branched silicone resins of the invention are particularly effective in increasing the fire resistance of polycarbonates and blends of polycarbonate with other resins such as polycarbonate/ABS blends.

**[0052]** Applications include but are not limited to transportation vehicles, construction, electrical application, printed circuits boards and textiles. Unsaturated polyester resins, or epoxy are moulded for use in, for example, the nacelle of wind turbine devices. Normally, they are reinforced with glass (or carbon) fibre cloth, however, the use of a flame retardant additive is important for avoiding fire propagation.

35

**[0053]** The branched silicone resins of the invention frequently have further advantages including but not limited to transparency, higher impact strength, toughness, increased adhesion between two surfaces, increased surface adhesion and improved tensile and flexural mechanical properties. The resins can be added to polymer compositions to  
5 improve mechanical properties such as impact strength, toughness and tensile and flexural mechanical properties. The resins can be used to treat reinforcing fibres used in polymer matrices to improve adhesion at the fibre polymer interface. The resins can be used at the surface of polymer compositions to improve adhesion to paints.

10 **[0054]** The branched silicone resins of the invention can for example be present in thermoplastic, thermoset or rubber organic polymer compositions in amounts ranging from 0.1 or 0.5% by weight up to 50 or 75%. Preferred amounts may range from 0.1 to 25% by weight silicone resin in thermoplastic or rubber compositions such as polycarbonates, and from 0.2 to 75% by weight in thermosetting compositions such as epoxy resins.

15 **[0055]** In an alternative method according to the invention for increasing the fire resistance of a thermoplastic, thermoset or rubber organic polymer composition, for example a polycarbonate or blend of polycarbonate such as a polycarbonate/ABS blend, a branched silicone resin containing at least one group selected from phosphonate and phosphinate  
20 groups and a branched silicone resin containing at least one organic group containing nitrogen is added to the thermoplastic, thermosetting or rubber organic polymer composition. The invention thus includes a thermoplastic, thermoset or rubber organic polymer composition comprising a thermoplastic, thermoset or rubber organic polymer, a branched  
25 silicone resin containing at least one group selected from phosphonate and phosphinate groups and a branched silicone resin containing at least one organic group containing nitrogen. The weight ratio of branched silicone resin containing at least one group selected from phosphonate and phosphinate groups to branched silicone resin containing at least one  
30 organic group containing nitrogen can for example be in the range 0:10 to 9:1 by weight. The invention extends thus to thermoplastic, thermoset or rubber organic polymer comprising a thermoplastic, thermoset or rubber organic polymer and a branched silicone  
resin containing at least one organic group containing nitrogen.

**[0056]** The total amount of branched silicone resins present in the thermoplastic, thermoset or rubber organic polymer compositions can for example be in the range from 0.1  
35 or 0.5% by weight up to 50 or 75% as described above. It is however preferred to use a

branched silicone resin according to the invention containing at least one group selected from phosphonate and phosphinate groups and at least one organic group containing nitrogen. Such a resin containing phosphorus and nitrogen more reliably achieves improved fire resistance and intumescence.

5

**[0057]** The branched silicone resins of the invention can alternatively be used as a fire resistant coating. The resins can be applied to a wide variety of substrates including plastics, metal, textile, paper and wood substrates, and are particularly effective when applied to structural elements such as walls, columns, girders and lintels as they form an expanded char, behaving as an intumescent material, when exposed to a fire. This expanded (foamed) char acts as an insulating material which limits transfer of heat to adjacent rooms in a fire and protects structural elements so that they do not reach a temperature at which they are weakened, or reach that temperature more slowly. The branched silicone resins are soluble in polar organic solvents such as ketones, for example methyl isobutyl ketone or methyl isoamyl ketone, and aromatic hydrocarbons such as toluene, xylene or trimethylbenzene. The branched silicone resins can be the only polymers in the coating or can be mixed with a film-forming binder such as an epoxy resin, a polyurethane or an acrylic polymer. The resins can be dissolved in an appropriate solvent for use as a fire resistant coating. The dissolved branched silicone resins can be applied by dip-, spin-, spray-coating, etc. on a wide variety of substrates (plastics, textiles, paper, metal, wood, cork, etc.), or as fibre sizing agents, or in filler (aluminium tetrahydrate, ATH, magnesium dihydrate, MDH) treatment, or in carbon nanotube functionalisation.

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**[0058]** Compositions containing the branched silicone resins of the invention, or the thermoplastic, thermoset or rubber organic polymer compositions containing a branched silicone resin containing at least one group selected from phosphonate and phosphinate groups and a branched silicone resin containing at least one organic group containing nitrogen, can contain additives such as fillers, pigments, dyes, plasticisers, adhesion promoters, impact resistants, hardeners (e.g. for anti-scratch), coupling agents, antioxidants and/or light stabilisers. Such additives may be used in thermoplastic, thermoset or rubber organic polymer compositions and in coating compositions.

35

**[0059]** In particular the thermoplastic, thermoset or rubber organic polymer compositions of the invention can contain a reinforcing filler such as silica. The silica is preferably blended with the branched silicone resin of the invention, or with the branched silicone resin



containing at least one group selected from phosphonate and phosphinate groups and the branched silicone resin containing at least one organic group containing nitrogen, before the resin(s) is added to the thermoplastic, thermoset or rubber organic polymer composition.

When the resin is heated with the silica in the thermoplastic, thermoset or rubber organic

5 polymer composition, there some bonding may take place between the resin and the silica.

The silica can for example be present at 0.1 or 0.5% by weight up to 40 or 60% by weight of the thermoplastic, thermoset or rubber organic polymer composition, and can be present at 1 to 500% by weight based on the branched silicone resin.

10 **[0060]** The thermoplastic, thermoset or rubber organic polymer compositions of the invention can contain a silicone gum, that is a high molecular weight substantially linear polydiorganosiloxane. The silicone gum can for example be a polydimethylsiloxane of viscosity at least 60,000 centiStokes, particularly above 100,000 cSt, and may have a viscosity as high as 30,000,000 cSt. The silicone gum is preferably blended with the

15 branched silicone resin of the invention, or with the branched silicone resin containing at least one group selected from phosphonate and phosphinate groups and the branched silicone resin containing at least one organic group containing nitrogen, before the resin(s) is added to the thermoplastic, thermoset or rubber organic polymer composition. The silicone gum can for example be present at 0.1 or 0.5% by weight up to 20 or 30% by weight of the

20 thermoplastic, thermoset or rubber organic polymer composition, and can be present at 1 to 100% by weight based on the branched silicone resin. The silicone gum acts as a plasticiser for the branched silicone resins and may increase the flexural strength of thermoplastic, thermoset or rubber organic polymer compositions containing the branched silicone resins.

25 **[0061]** If silica is incorporated in compositions comprising the branched silicone resins as described above, it can be gum-coated silica. Gum-coated silica is sold by Dow Corning under the trademarks DC 4-7051 and DC 4-7081 as a resin modifier for silicone resins.

**[0062]** The invention is illustrated by the following Examples

30

### **Example 1**

**[0063]** In a round bottomed flask equipped with a magnetic stirrer and placed under nitrogen, 20 gr of vinyl dimethylphosphonate (0.147 moles) were introduced followed by 32.5

35 gr of aminopropyltriethoxysilane (sold by Dow Corning under the trade mark Z-6011; 0.147

moles) in 100 gr ethanol. The solution was heated at 75 °C for 12 hours under nitrogen. The reaction was cooled down to room temperature and the ethanol was removed under high vacuum. The product is believed to be mainly 3-(2-dimethylphosphonatoethylamino)propyltriethoxysilane.

5

**[0064]** The hydrolysis and condensation of this trialkoxysilane was conducted at room temperature under high vacuum to obtain an aminophosphorylated branched silicone resin, believed to be a T-resin containing N-(2-dimethylphosphonatoethyl)aminopropyl groups, as a white solid.

10

**[0065]** 3.24 g of the branched silicone resin prepared above was added to 300 g of polycarbonate in an internal mixer compounder at 270 °C. The residence time in the mixer was 8 minutes. The composition obtained was pressed in a hot press machine at 250 °C and 100 MPa.

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**[0066]** The resulting polycarbonate composition was subjected to conventional thermogravimetric analysis in which the sample was heated to 950°C at a heating rate of 10°C per minute. The residue remaining at 950°C was 30.1%, indicating formation of a considerable amount of ceramic char. By comparison, a sample of the polycarbonate without the silane additive had a residue of 1.24% at 950°C.

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**[0067]** The polycarbonate containing the branched silicone resin of Example 1 was also subjected to flash thermogravimetric analysis in which the sample was heated to 500°C at a heating rate of 300°C per minute and held at 500°C for 20 minutes. This test simulates exposure of the composition to a fire. The residue remaining after 20 minutes at 500°C was 68.5%, indicating formation of a large amount of char. By comparison, a sample of the polycarbonate without the silane additive had a residue of 11.7% after 20 minutes at 500°C.

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### **Example 2**

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**[0068]** In a reaction flask heated up at 80°C, under inert atmosphere (N<sub>2</sub> pressure), 20 gr of the vinyl end-capped PDMS (2-7463) (2.6%wtVi, 0.0192mols Vi) are introduced, followed by 2.65 gr (0.0192 mols) of diethylphosphite. Finally, 0.31 gr of AIBN (0.0019 mols) were added and the reaction mixture stirred at 80°C for 16 hours. The reaction was cooled down

and the crude analyzed by mean of  $^{29}\text{Si}$  and  $^{31}\text{P}$ NMR. It clearly shows the disappearance of the vinyl and P-H functionalities and the formation of the Si-CH<sub>2</sub>-CH<sub>2</sub>-P bond.

### Example 3

#### 5 Synthesis description of $\text{T}_{25}^{\text{DOPO}}\text{T}_{5}^{\text{Bz}}\text{T}_{50}^{\text{Ph}}\text{T}_{20}^{\text{Me}}$ siloxane resin

[0069] In a 700 ml reactor equipped with condenser, KPG stirrer and distillation unit, 148.5 g of Phenyltrimethoxysilane (0.75 mol), 40.8g of methyltrimethoxysilane (0.3 mol), 136.43 g (0.375 mol) of DOPO-trimethoxysilane, and 24.56 g (0.075 mol) of Methoxy-  
10 benzoxazinepropyltrimethoxysilane were mixed under vigorous stirring. Then 33.75 g of distilled water was added and the mixture was heated under stirring to 80 degrees C for 1 h. Then the reflux condenser was removed and replaced with the distillation condenser which is connected to a diaphragm pump system. A vacuum of 450 mbar was slowly applied while the distillation of methanol has started. The temperature of the vessel was raised to around  
15 110 deg C for around 3 h and methanol removed until the distillation temperature finally dropped. While still warm (at around 100 deg C) the highly viscous yellow material was poured into a HDPE container for storage. Around 264.6 g of a finally nearly glassy material was received.

20 [0070] 9.64 g of the  $\text{T}_{25}^{\text{DOPO}}\text{T}_{5}^{\text{Bz}}\text{T}_{50}^{\text{Ph}}\text{T}_{20}^{\text{Me}}$  siloxane resin prepared were added to 312 g of polycarbonate in an internal mixer compounder at 270 °C. The residence time in the mixer was 8 minutes. The matter obtained was pressed in a hot press machine at 250 °C and 100 MPa.

25 The composition of Example 3 was subjected to the UL-94 Vertical Burn test in which a flame is applied to the free end of a 120mm x 12mm sample. The sample was self-extinguishing with a flaming time (average t<sub>1</sub>) of 8 seconds and did not exhibit dripping (UL-94 V0 rating at 1.5 mm).

#### 30 Comparative Examples

[0071] Example 3 was repeated replacing the  $\text{T}_{25}^{\text{DOPO}}\text{T}_{5}^{\text{Bz}}\text{T}_{50}^{\text{Ph}}\text{T}_{20}^{\text{Me}}$  siloxane resin by:  
C1 - reference sample with no additive (neat polycarbonate)

[0072] The sample (C1) consisting solely of polycarbonate (neat polycarbonate, without any additive) exhibited dripping with ignition of the cotton placed below the sample and an average flaming time  $t_1$  of 11 seconds, and therefore a UL-94 V2 classification.

5 [0073] The composition of Example 3 was also subjected to Cone Calorimetry analyses and compared with the reference sample (neat polycarbonate). By this technique it was possible to determine the MAHRE value, which is closely related to the heat release rate value. It was found to be decreased by 16.3% compared to the reference sample (C1). AHRE(t), the Average Rate of Heat Emission at time t, is defined as the cumulative heat  
10 emission per unit area of exposed specimen, from  $t=0$  to  $t=t$ , divided by t. MAHRE is the maximum value of ARHE during that time period.

#### Example 4

##### Synthesis description of DOPO-Bz silane.

15

[0074] In a 250ml flask, equipped with a nitrogen inlet, a condenser, and a magnetic stirrer, 13.26gr (0.06mol, 1eq) of Aminopropyltriethoxysilane (Z-6011), 7.32g (0.06mol, 1eq) of 2-hydroxybenzaldehyde, 12.96gr (0.06mol, 1eq) DOPO and 120gr methanol were mixed together. The reaction mixture was stirred at room temperature for 12 h. After, 4.92 g (0.06  
20 mol, 1eq) of 37% formaldehyde was added and the mixture was stirred at room temperature for 6 h and finally refluxed for a further 12h. The methanol solution was cooled down and the product was drummed off.

#### Example 4a

25 Preparation of PC + 0.5wt% DOPO- Benzoxazine siloxane resin ( $T_{30}^{DOPO-Bz}$   $T_{50}^{Ph}$   $T_{20}^{Me}$ )

[0075] 1.61 g of the DOPO-Bz siloxane resin prepared was added to 321.6 g of polycarbonate in an internal mixer compounder at 270 °C. The residence time in the mixer was 8 minutes. The matter obtained was pressed in a hot press machine at 250 °C and 100  
30 MPa.

#### Example 4b

Preparation of PC + 2.5wt% DOPO- Benzoxazine siloxane resin ( $T_{30}^{DOPO-Bz}$   $T_{50}^{Ph}$   $T_{20}^{Me}$ )

**[0076]** 8.04 g of the DOPO-Bz siloxane resin prepared were added to 314.2 g of polycarbonate in an internal mixer compounder at 270 °C. The residence time in the mixer was 8 minutes. The matter obtained was pressed in a hot press machine at 250 °C and 100 MPa.

5

**[0077]** The compositions of Examples 4a and 4b were subjected to the UL-94 Vertical Burn test in which a flame is applied to the free end of a 120mm x 12mm sample. The samples were self-extinguishing with similar flaming times (average  $t_1$ ) of ca. 5 seconds and did not exhibit dripping (UL-94 V0 rating at 1.5 mm). On the other hand, a sample consisting solely of polycarbonate (neat polycarbonate, without any additive), sample C1, exhibited dripping with ignition of the cotton placed below the sample and an average flaming time  $t_1$  of 11 seconds, and therefore a UL-94 V2 classification.

10

**[0078]** The compositions of Examples 4a and 4b were also subjected to Cone Calorimetry analyses and compared with the reference sample (neat polycarbonate). The table below shows the benefit of adding the DOPO-Benzoxazine siloxane resin to polycarbonate. It leads to a delay in the ignition (longer time to ignition), to a lower peak of heat release rate, to a higher "Fire Performance Index" meaning a less hazardous fire and to a lower smoke emission. The doped sample exhibited as well a stronger intumescent behaviour and the resulting char column appeared to be mechanically stronger than for neat PC.

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**[0079]** Cone Calorimeter\* test results at heat flux of 50 kWm<sup>-2</sup> on 2 mm thickness plates

	C1 (Reference: neat PC)	Example 4b
Impact resistance (J/m)	1925	1848
Time to ignition (s)*	66	73
pHRR (kWm <sup>-2</sup> )*	700	611
Smoke parameter (MWKg <sup>-1</sup> )*	429	373
Fire Performance Index*	0.09	0.12
Intumescence (mm)*	50	70

(fire performance index =  $t_i/pHRR$ ; the higher, the better)

25

[0080] Mechanical impact tests were carried out on the reference sample (neat PC) and sample of Example 4b, showing that the presence of DOPO-Benzoxazine siloxane resin, at 2.5wt%, does not significantly affect the impact resistance of polycarbonate.

5 Tg values, by Differential Scanning Calorimetry, were found to slightly decrease from 150 °C to 146 °C, for 0.5 and 2.5wt% of such siloxane resin. A loading of 0.5-2.5 wt% is found here to be a good compromise between FR and mechanical performance.

### **Example 5**

10 **Preparation of PC + 3 wt% DOPO- aryl amino siloxane resin (T<sup>DOPO-arylamino</sup><sub>30</sub> T<sup>Ph</sup><sub>50</sub> T<sup>Me</sup><sub>20</sub>)**

[0081] 9.69 g of the DOPO-arylamino siloxane resin prepared were added to 311.58 g of polycarbonate in an internal mixer compounder at 270 °C. The residence time in the mixer was 8 minutes. The matter obtained was pressed in a hot press machine at 250 °C and 100  
15 MPa.

### **Example 6**

**Preparation of PC + 3 wt% DOPO- aryl amino siloxane resin (T<sup>DOPO-arylamino</sup><sub>30</sub> T<sup>Ph</sup><sub>50</sub> T<sup>Me</sup><sub>20</sub>)  
+ 0.5wt% potassium diphenylsulfone sulfonate (KSS)**

20 [0082] 9.58 g of the DOPO-Bz siloxane resin prepared and 1.58 g of KSS were added to 309.9 g of polycarbonate in an internal mixer compounder at 270 °C. The residence time in the mixer was 8 minutes. The matter obtained was pressed in a hot press machine at 250 °C and 100 MPa.

25

### **Comparative Examples**

[0083] Example 5 was repeated replacing the DOPO- aryl amino siloxane resin (T<sup>DOPO-arylamino</sup><sub>30</sub> T<sup>Ph</sup><sub>50</sub> T<sup>Me</sup><sub>20</sub>) by:

30

[0084] C2 - 0.5 wt% potassium diphenylsulfone sulfonate (KSS)

[0085] Both samples, Example 5 and 6, exhibit the same MAHRE value, however sample 6 (with DOPO-arylamino siloxane resin and KSS) exhibits the lowest peak of heat release  
35 rate.

**[0086]** Cone Calorimeter\* test results at heat flux of 50 kWm<sup>-2</sup> on 4 mm thickness plates

Sample	Peak of heat release rate (kWm <sup>-2</sup> )	MAHRE (KW)	Heat release rate (KW/m <sup>2</sup> )
C1	444.1	240.6	228.4
C2	399.9	248.7	270.7
Example 5	358.7	202.9	218.6
Example 6	293.5	202.5	202.1

**[0087]** We observe, in sample C2, that the addition of KSS at 0.5wt% (typical amount for maintaining the transparency of the polycarbonate sample) did not decrease the MAHRE and Heat Release Rate values, on the contrary they were further increased compared to neat PC, as seen in the Table below. KSS is typically used, together with PTFE, for inhibiting dripping and therefore achieving a UL-94 V0 classification. However, in terms of Heat Release Rate or MAHRE decrease, it is not working by itself. On the other hand, sample of Example 5 was found to lead to a decrease of the 3 parameters here evaluated, being such decrease even further intense when the DOPO- arylamino siloxane resin is used together with KSS (Example 6). There is, therefore, a synergy when KSS and DOPO-arylamino siloxane resin are employed as FR additives in PC matrix.

#### 15 **Example 7**

##### **Synthesis description of DOPO-aryl amino siloxane resin (T<sup>DOPO</sup><sub>30</sub> T<sup>Z6883</sup><sub>10</sub> T<sup>Ph</sup><sub>40</sub> Q<sub>20</sub>)**

**[0088]** In a reactor, 102g of DOPO-trimethoxysilane, 23.79gr of phenyltrimethoxysilane and 38.81gr of tetraethoxysilane were diluted in 204gr of toluene and heated to 75°C. Once the temperature of 75°C was reached, a mixture of 53.74gr water and 53.74gr methanol was added. The solution was refluxed for 2 hours. After cooling down to room temperature, the mixture was filtered and the low volatiles were removed under reduced pressure (68mm Hg @ 100°C) using a rotary evaporator. The obtained resin was further dried under a 30mmHg vacuum for 2 hours at 100°C to recover 164.2gr of the desired resin as a pale yellow solid.

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##### **Synthesis description of aryl amino siloxane resin (T<sup>Z6883</sup><sub>50</sub> T<sup>Ph</sup><sub>50</sub>)**

**[0089]** In a reactor, 433.5 g of Z-6883, 336.6 g of Phenyltrimethoxysilane, and 0.45 g (400 ppm) of a 1N potassium hydroxide solution were mixed. Still at room temperature 183.6 g of

water and 183.6 g of methanol were added. The mixture was heated then to 70 degrees Celsius and kept under reflux conditions for 1 hour. Removed methanol and water at atmospheric pressure until the reaction mixture temperature rises up to about 70 degree Celsius. Added constantly toluene and continue removal of methanol and water by  
 5 azeotropic distillation while keeping the toluene concentration at about 50 wt%. When the temperature reached around 110 degrees Celsius the mixture was allowed to reflux for around 6 hours. After cooling down to room temperature, the mixture was neutralized with 0.44 g of acetic acid. Then the solution was filtered and the solvent was removed in vacuum and 535.5 g of a colourless solid was received

10

**Example 7a****Preparation of PC + 10wt%  $T^{\text{DOPO}}_{30} T^{\text{Z6883}}_{10} T^{\text{Ph}}_{40} Q_{20}$** 

15

[0090] 32 g of the DOPO-Bz siloxane resin prepared was added to 286 g of polycarbonate in an internal mixer compounder at 270 °C. The residence time in the mixer was 8 minutes. The matter obtained was pressed in a hot press machine at 250 °C and 100 MPa.

**Example 7b****Preparation of PC + 15wt%  $T^{\text{Z6883}}_{50} T^{\text{Ph}}_{50}$** 

20

[0091] 47.7 g of the DOPO-Bz siloxane resin prepared was added to 268 g of polycarbonate in an internal mixer compounder at 270 °C. The residence time in the mixer was 8 minutes. The matter obtained was pressed in a hot press machine at 250 °C and 100 MPa.

25

[0092] Samples of Examples 7a and 7b were analysed by thermal gravimetric analyses, differential scanning calorimetry and Cone Calorimetry.

30

[0093] These resins were prepared with a commercial silane (phenyl amino silane, Dow Corning® Z6883). The MAHRE value was found to decrease from 240.6 kW to 193.1 kW when doped at 10wt% with  $T^{\text{DOPO}}_{30} T^{\text{Z6883}}_{10} T^{\text{Ph}}_{40} Q_{20}$ , and to 200.7 kW when doped at 15wt% with  $T^{\text{Z6883}}_{50} T^{\text{Ph}}_{50}$ . There was a decrease in MAHRE with both types of FR additives, however, the presence of phosphorus (DOPO) is found to increase the efficiency of the FR additive.



**[0094]** The Table below shows the different parameters evaluated for samples of Examples 7a and 7b. Also, the amount of Si, P, N and phenyl groups (Ph) was calculated in order to correlate this with the MAHRE value and Tg.

Sample	Tg	Thermal degrad. onset	MAHR E	wt%			
				Si	N	P	Ph
C1 (Reference: neat PC)	151.5	479.4	240.6	--	--	--	--
Example 7a	145.0	438.6	193.1	1.440	0.07 2	0.478	4.356
Example 7b	151.4	444.2	200.7	2.316	0.57 9	--	6.370

5

**[0095]** The decrease of Tg was found to result from the presence of phosphorus. Si and Ph have no effect on Tg and lead to the increase of the thermal degradation onset. In fact, the siloxane formation promotes cross-linking, which is beneficial to the flame extinguishing behaviour. Contrary to what was expected, a high thermal degradation onset was found not to lead to a low MAHRE. In fact, the opposite was observed. The simultaneous presence of P and N species (P-N synergy) was found to play a major role in the MAHRE value decrease. Moreover, the P-free solution, despite presenting a decreased MAHRE value compared to neat PC, was not as efficient as the SiPN based solutions.

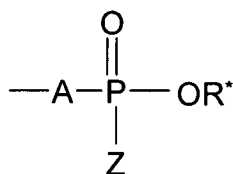
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**[0096]** Sample of Example 7b was also analyzed by the UL-94 Vertical Burn test. It is classified as UL-94 V1 because, despite the dripping inhibition observed, the flaming time is not short enough to reach the V0 rating.

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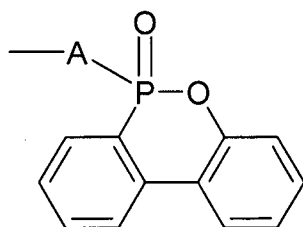
**CLAIMS**

1. A branched silicone resin containing at least one group selected from phosphonate and phosphinate groups and at least one organic group containing nitrogen.
2. A branched silicone resin according to Claim 1, characterized in that the resin contains at least one phosphonate or phosphinate moiety present in a M unit of the formula  $RPR_2SiO_{1/2}$  and/or D unit of the formula  $RPRSiO_{2/2}$  and/or a T unit of the formula  $RPSiO_{3/2}$ , where RP is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent, and each group R is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms.
3. A branched silicone resin according to Claim 2, characterized in that the phosphonate or phosphinate group is present in a T unit of the formula  $RPSiO_{3/2}$ .
4. A branched silicone resin according to Claim 2 or Claim 3, characterized in that the group RP has the formula



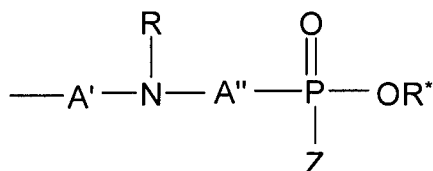
where A is a divalent hydrocarbon group having 1 to 20 carbon atoms, R\* is an alkyl or aryl group having 1 to 12 carbon atoms, and Z is a group of the formula  $-\text{OR}^*$  or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms.

5. A branched silicone resin according to Claim 2 or Claim 3, characterized in that the group RP has the formula



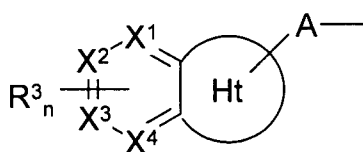
where A is a divalent hydrocarbon group having 1 to 20 carbon atoms.

6. A branched silicone resin according to any of Claims 1 to 3, characterized in that the phosphonate or phosphinate group and the organic group containing nitrogen are both present in a group of the formula



where A' is a divalent organic group having 1 to 20 carbon atoms, A'' is a divalent organic group having 1 to 20 carbon atoms, R\* is an alkyl group having 1 to 12 carbon atoms and Z is a group of the formula  $\text{---OR*}$  or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 12 carbon atoms, or R\* and Z can be joined to form a heterocyclic ring, and R is hydrogen or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 12 carbon atoms, or can be joined to A'' to form a heterocyclic ring.

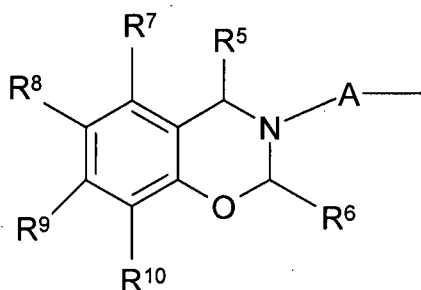
7. A branched silicone resin according to any of Claims 1 to 5, characterized in that the organic group containing nitrogen is a heterocyclic group present as a group of the formula



where X1, X2, X3 and X4 independently represent a CH group or a N atom and form a benzene, pyridine, pyridazine, pyrazine, pyrimidine or triazine aromatic ring, Ht represents a heterocyclic ring fused to the aromatic ring and comprising 2 to 40 carbon atoms, 1 to 4 nitrogen atoms and optionally 1 or 2 oxygen and/or sulphur

atoms; A represents a divalent organic linkage having 1 to 20 carbon atoms bonded to a nitrogen atom of the heterocyclic ring; the heterocyclic ring can optionally have one or more substituent groups selected from alkyl, substituted alkyl, cycloalkyl, alkenyl, alkynyl, aryl and substituted aryl groups having 1 to 12 carbon atoms and amino, nitrile, amido and imido groups; and R<sub>3n</sub>, with n = 0 – 4, represents an alkyl, substituted alkyl, alkenyl group having 1 to 8 carbon atoms or cycloalkyl, alkynyl, aryl, substituted aryl groups having 1 to 40 carbon atoms, or an amino, nitrile, amido or imido group or a carboxylate –C(=O)-O-R<sub>4</sub>, oxycarbonyl –O-(C=O)-R<sub>4</sub>, carbonyl –C(=O)-R<sub>4</sub>, or an oxy –O-R<sub>4</sub> substituted group with R<sub>4</sub> representing hydrogen or an alkyl, cycloalkyl, alkenyl, alkynyl, aryl, or substituted aryl groups having 1 to 40 carbon atoms, substituted on one or more positions of the aromatic ring, or two groups R<sub>3</sub> can be joined to form a ring system comprising at least one carbocyclic or heterocyclic ring fused to the aromatic ring.

8. A branched silicone resin according to Claim 7, characterised in that the heterocyclic group is a benzoxazine group of the formula



where R<sub>5</sub> and R<sub>6</sub> each represent hydrogen, an alkyl, substituted alkyl, cycloalkyl, alkenyl, alkynyl, aryl or substituted aryl group having 1 to 12 carbon atoms, or an amino or nitrile group; and R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub> and R<sub>10</sub> each represent hydrogen, an alkyl, substituted alkyl, alkenyl group having 1 to 8 carbon atoms or cycloalkyl, alkynyl, aryl or substituted aryl group having 1 to 40 carbon atoms, or an amino, nitrile, amido or imido group or a carboxylate –C(=O)-O-R<sub>4</sub>, oxycarbonyl –O-(C=O)-R<sub>4</sub>, carbonyl –C(=O)-R<sub>4</sub>, or an oxy –O-R<sub>4</sub> substituted group with R<sub>4</sub> representing hydrogen or an alkyl, cycloalkyl, alkenyl, alkynyl, aryl, or substituted aryl groups having 1 to 40 carbon atoms, substituted on one or more positions of the benzene ring, or R<sub>7</sub> and R<sub>8</sub>, R<sub>8</sub> and R<sub>9</sub> or R<sub>9</sub> and R<sub>10</sub> can each be joined to form a ring

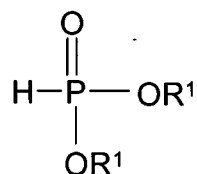
system comprising at least one carbocyclic or heterocyclic ring fused to the benzene ring.

9. A branched silicone resin according to any of Claims 1 to 5, characterized in that the organic group containing nitrogen comprises an aminoalkyl or aminoaryl group bonded to a silicon atom of the silicone resin.
10. A process for the preparation of a branched silicone resin according to Claim 1, characterized in that at least one alkoxysilane of the formula  $RPSi(OR')_3$ ,  $RPR_{11}Si(OR')_2$  or  $RPR_{11}SiOR'$ , at least one alkoxysilane of the formula  $RNSi(OR')_3$ ,  $RNR_{12}Si(OR')_2$  or  $RNR_{12}SiOR'$ , and optionally one or more alkoxysilane of the formula  $Si(OR')_4$ ,  $R_4Si(OR')_3$ ,  $R_4Si(OR')_2$  or  $R_4SiOR'$ , where each  $R'$  is an alkyl group having 1 to 4 carbon atoms; each  $R_p$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent; each  $R_{11}$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent; each  $R_N$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing an organic nitrogen substituent; each  $R_{12}$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing an organic nitrogen substituent; and each  $R_4$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms, are hydrolysed and condensed to form siloxane bonds.
11. A process for the preparation of a branched silicone resin according to Claim 1, characterized in that at least one alkoxysilane of the formula  $RPRNSi(OR')_2$  or  $RPRNR_{13}SiOR'$ , at least one alkoxysilane of the formula  $Si(OR')_4$ ,  $R_4Si(OR')_3$ ,  $RPSi(OR')_3$ ,  $RNSi(OR')_3$ , and optionally one or more alkoxysilane of the formula  $R_4Si(OR')_2$ ,  $R_4SiOR'$ ,  $RPR_{11}Si(OR')_2$ ,  $RPR_{11}SiOR'$ ,  $RNR_{12}Si(OR')_2$  or  $RPR_{12}SiOR'$ , where each  $R'$  is an alkyl group having 1 to 4 carbon atoms; each  $RP$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent; each  $R_N$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing an organic nitrogen substituent; each  $R_{13}$  is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl

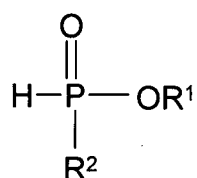
group having 1 to 20 carbon atoms or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent or an organic nitrogen substituent; each R<sub>4</sub> is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms; each R<sub>11</sub> is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent; and each R<sub>12</sub> is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing an organic nitrogen substituent, are hydrolysed and condensed to form siloxane bonds.

12. A process for the preparation of a branched silicone resin according to Claim 1, characterized in that at least one alkoxy silane of the formula  $R_bSi(OR')_3$ ,  $R_bR_{13}Si(OR')_2$  or  $R_bR_{13}SiOR'$ , and optionally one or more alkoxy silane of the formula  $Si(OR')_4$ ,  $R_4Si(OR')_3$ ,  $R_4R_{12}Si(OR')_2$ ,  $R_4R_{12}SiOR'$ ,  $RPSi(OR')_3$ ,  $RPR_{11}Si(OR')_2$ ,  $RPR_{11}SiOR'$ ,  $RNSi(OR')_3$ ,  $RNR_{12}Si(OR')_2$  or  $RNR_{12}SiOR'$ , where each R' is an alkyl group having 1 to 4 carbon atoms, each R<sub>b</sub> is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing both a phosphonate or phosphinate substituent and an organic nitrogen group; each R<sub>13</sub> is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent and/or an organic nitrogen group; RP is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent; RN is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing an organic nitrogen substituent; each R<sub>4</sub> is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms, each R<sub>11</sub> is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing a phosphonate or phosphinate substituent; and each R<sub>12</sub> is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms containing an organic nitrogen substituent, is hydrolysed and condensed to form siloxane bonds.

13. A process for the preparation of an organopolysiloxane containing a phosphonate or phosphinate group, characterized in that an organopolysiloxane containing an olefinically unsaturated group is reacted with a phosphite of the formula

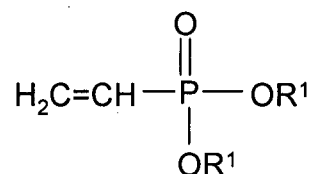


or a phosphinate of the formula

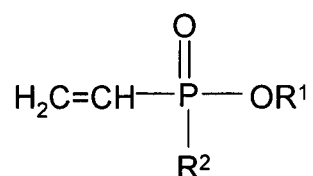


where each R1 is an alkyl or aryl group having 1 to 12 carbon atoms, and R2 is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms, in the presence of a free radical initiator.

14. A process for the preparation of an organopolysiloxane containing a phosphonate or phosphinate group, characterized in that an organopolysiloxane containing a primary or secondary amino group is reacted with an olefinic phosphite of the formula



or an olefinic phosphinate of the formula



where each R1 which can be the same or different is an alkyl group having 1 to 12 carbon atoms, and R2 is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl group having 1 to 20 carbon atoms.

15. Use of a branched silicone resin as claimed in any of Claims 1 to 9 in a thermoplastic, thermosetting or rubber organic polymer composition to reduce the flammability of the organic polymer composition.
16. Use of a branched silicone resin as claimed in any of Claims 1 to 9 as a fire resistant coating on a substrate.
17. A thermoplastic, thermoset or rubber organic polymer composition comprising a thermoplastic, thermoset or rubber organic polymer and a branched silicone resin as claimed in any of Claims 1 to 9.
18. A thermoplastic, thermoset or rubber organic polymer composition comprising a thermoplastic, thermoset or rubber organic polymer, a branched silicone resin containing at least one organic group containing nitrogen, and, preferably, a branched silicone resin containing at least one group selected from phosphonate and phosphinate groups.
19. An organic polymer composition according to Claim 17 or Claim 18 wherein the thermoplastic organic polymer comprises a polycarbonate or a blend of polycarbonate with another organic polymer.
20. A polymer composition according to any of Claims 17 to 19 characterised in that the composition contains a filler.
21. The filler of claim 20 can be treated with an alkoxysilane or with a branched silicon resin as defined in any of Claims 1 to 9.
22. An organic polymer composition according to any of Claims 17 to 21 characterised in that the composition contains a silica filler.



23. An organic polymer composition according to any of Claims 17 to 22 characterised in that the composition also comprises a polydiorganosiloxane gum.
24. An organic polymer composition according to Claim 19 characterised in that the silica is coated with a polydiorganosiloxane gum.
25. A polymer composition according to any of Claims 17 to 24 characterised in that the composition contains another flame retardant additive.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/CN2011/000845

## A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

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)

IPC: C08G77/-;C08G77/26; C08G77/30; C08G77/388;C08G77/395

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)

WPI, EPODOC, CNPAT, CNKI, REGISTRY, CAPLUS phosphorus, phosphine, phosphinate, phosphonate, phosphate, +siloxane, +silicon?, nitrogen, +amino+silane?, +amine+silane?, amino, benzoxazine, benzoxazine+silane?, +vinyl+silane?, flam+, branch+, +trialkoxysilane?, +SiO<sub>3</sub>/2, +SiO<sub>1.5</sub> Searching for some structure formulas written in description of the present application

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN1509159A(DENTSPLY DETREY GMBH) 30 June 2004(30.06.2004) Example 1	1-3,12
X	SHU YIN, Synthesis of a Novel Phosphorus-Containing Flame Retardant and the Thermal Stability of Flame Retarded PC/ABS, Journal of Functional Polymer, 2008, No.2, Pages 159-163	1-5,9-11,13,15-25
X	WUDAN, Synthesis Characterization of a Novel Flame Retardant Containing Silicon and Its Application in PC/ABS Alloy, Polymer Materials Science & Engineering, 2008, No.3, Pages 125-128	1-3,6,15-25
X	CN101665573A(UNIV SICHUAN) 10 March 2010(10.03.2010) Claims 1,2	1-5,9-11,13
X	CN1974721A(UNIV SHANGHAI JIAOTONG) 06 June 2007(06.06.2007) Claims 1,2	1-3,6,15-25
X	XILEI CHEN, Preparation and Thermal Properties of a Novel flame-retardant Coating, Polymer Degradation and Stability, 2007, Vol. 92, Pages 1141-1150	1-3,12

Further documents are listed in the continuation of Box C.

See patent family annex.

<p>* Special categories of cited documents:</p> <p>“A” document defining the general state of the art which is not considered to be of particular relevance</p> <p>“E” earlier application or patent but published on or after the international filing date</p> <p>“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)</p> <p>“O” document referring to an oral disclosure, use, exhibition or other means</p> <p>“P” document published prior to the international filing date but later than the priority date claimed</p>	<p>“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</p> <p>“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</p> <p>“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</p> <p>“&amp;”document member of the same patent family</p>
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Date of the actual completion of the international search  
14 August 2011(14.08.2011)

Date of mailing of the international search report  
**25 Aug. 2011 (25.08.2011)**

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**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/CN2011/000845

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN101274998A(GUANGZHOU CHEM INST CHINESE ACAD) 01 October 2008(01.10.2008) Claims 1-5	1-3
A	YONGHONG LIU, Polybenzoxazine Containing Polysilsesquioxane: Preparation and Thermal Properties, Journal of Applied Polymer Science, 2006, Vol.99, Pages 927-936	1-25

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No. PCT/CN2011/000845
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Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
CN1509159A	30.06.2004	DE10206451A1	28.08.2003
		US2003187094A1	02.10.2003
		WO03070198A1	28.08.2003
		AU2003202999A1	09.09.2003
		EP1474094A1	10.11.2004
		JP2005517719T	16.06.2005
		US7041709B2	09.05.2006
		AU2009202780A1	30.07.2009
CN101665573A	10.03.2010	None	
CN1974721A	06.06.2007	CN100462418C	18.02.2009
CN101274998A	01.10.2008	None	

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2011/000845

## A. CLASSIFICATION OF SUBJECT MATTER

C08G77/30 (2006.01) i

C08G77/26 (2006.01) i

C08G77/388 (2006.01) i

C08G77/395 (2006.01) i

C08L83/04 (2006.01) i