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**Flame-resistant composition for manufacturing
electrical cables having insulating
and/or functional properties**

Description

The invention relates to compositions or compounds for manufacturing fire-proof cables having insulating and/or functional properties. The invention also relates to fire-proof cables having insulating and/or functional properties which are manufactured using such compositions or compounds.

Fire-proof cables are electrical cables which are also able to function in the event of fire, inter alia, over a certain period of time due to their constitution and should prevent conductance of fire in buildings via the cable. Maintaining the function of particularly relevant current circuits is of highest interest to guarantee adequate rescue and combating measures and damage limitation to people and valuables and to enable the teams of fire-fighters to combat the fire with greatest possible success. Furthermore, fire-proof cables must be designed such that low smoke development, lowest possible fire load and low pollution with toxic gases is guaranteed.

The criteria which fire-proof cables have to satisfy are controlled by law in many countries. Cables having reported insulation properties are thus tested for insulation failure, for example according to the International Standard IEC 331 or according to VDE 0472 Part 814 under the action of a flame at a test temperature of 750°C for a period of 180 minutes. This

test however only achieves the claims of reality in a very limited manner, since the temperature is only one criterion of many in an actual event of fire. Indeed, interaction of all factors of a fire incident must be considered, which also includes mechanical stress and additional requirements for the cable associated therewith.

Accordingly, the German regulations according to DIN 4102 Part 12 require a much more stringent test. This method is restricted not only to the "laboratory scale", but requires testing of a complete cable system under approximately realistic conditions in a test stand of at least 3 m length. Other influencing factors, such as for example mechanical forces acting on the cable, are also taken into account in this way. These may occur, for example due to deformations or partial failure of the support system or due to laying of the cables in curves caused by installation technology and the fastenings associated therewith. Furthermore, the ambient conditions are also included in the test. In addition, the composition of the oven atmosphere is changed as a result of the combustion of individual cable portions and other components present in the oven, for example of zinc coatings of the support device. In the test according to DIN 4102 Part 12, the cable is tested for the required safety regarding any short-circuit or an interruption in current flow (conductor interruption) according to a so-called unit temperature time curve (ETK; DIN 4102 Part 2) over a period of 90 minutes at temperatures up to 1,000°C. Functional property over a period of at least 90 minutes with exposure of the cable in the oven up to a temperature of 1,000°C is the highest class of functional property (E 90). Functional property of this category is required for cables, for example in plants for increasing water pressure for supplying extinguishing water, in ventilation plants in safety staircases, inner

staircases, lift wells and rooms for driving machinery of fire brigade lifts, in smoke and heat removal plants and in fire brigade lifts.

The use of flame-resistant polymer compounds having metal hydroxides, in particular aluminium hydroxide, as fillers is generally known for fire-proof cables. In order to achieve a maximum flame-protective effect, the aim is as high as possible a filler concentration. Polymers suitable for this purpose are, for example polyolefins, ethylene copolymers, organosilicon polymers or mixtures of such polymers. In the event of fire these filled polymer compositions should firstly prevent expansion of the fire along the cable, and secondly assume a protective function for the insulated wires. Flame-resistant compositions, as described in German 4 437 596 or European application 0 708 455, based on organosilicon polymers with ceramisable fillers, to which a wetting agent for the filler, for example metal soaps, such as aluminium soaps, is added, correspond to the closest state of the art and show the hitherto greatest flame-protective effect (functional property class E 90) with acceptable expense in terms of processing and cost. The specially added wetting agent thus has the aim, firstly of guaranteeing maximum content of ceramising filler with additionally adjustable viscosity, and secondly of guaranteeing a special linking effect between ceramising filler and the polymer matrix.

Further flame-inhibiting thermoplastic compositions with high quantity of filler are described in European application 0 054 424 and European application 0 082 407 and World 93/2056, and are based for example on the use of ethylene vinyl acetate and aluminium hydroxide and are used when manufacturing fire-resistant cables, inter alia, for the petrochemical industry. However, one disadvantage of such filled polymers consists generally

in a protective effect of limited duration, which subsides rapidly particularly at high temperatures and within a few minutes leads to destruction of all existing polymer structures, including wire insulation. The last-mentioned materials therefore cannot be used in areas where high functional property, for example functional property class E 90, caused by particular requirements is necessary, so that their use is restricted to fields of fewer critical requirements.

In order to guarantee an insulation and/or functional property for the electrical cables in the event of fire, high temperature-resistant materials are used. In this context insulating layers based on silicate fibres or silicone rubber are known. Use is made here of the electrically insulating property and the thermal resistance of silicon dioxide (SiO_2), which is produced when combusting (pyrolysis) organosilicon compounds. Hence the German Utility Model G 81 09 304 describes electrical cables, the wires of which surrounded by a sheath have double-layer insulation comprising an external insulating layer of a thermoplastic or elastomeric insulating material, such as for example ethylene vinyl acetate, and an inner insulating layer of extruded silicone rubber.

German Utility Model G 92 16 599 also describes electrical cables, the conductors of which are surrounded by a silicone rubber and a non-crosslinked ethylene vinyl acetate as the wire cover; a band with ceramic material applied is wound on this wire cover as a flame barrier. However, such insulation also does not permit a functional property which satisfies particularly high requirements.

German Offenlegungsschrift 3 713 267 describes flame-resistant compositions based on silicone rubber in castable form or a form which can be cured to form an

elastomer, which contain finely divided titanium dioxide and optionally silicon dioxide, catalytic quantities of finely divided platinum and an extinguishing substance, such as sodium bicarbonate. The latter releases carbon dioxide into the elastomer as a fire-inhibiting extinguishing gas which foams the elastomer below its decomposition temperature to give a mechanically stable microporous material. The mechanical strength of the foam structure is determined by the presence of the titanium dioxide which is present in a quantity of about five parts by weight per 100 parts by weight of silicone rubber. Electrically insulating components manufactured from such materials have a longer ability to function in the event of fire and improved creep resistance, but still do not always satisfy higher requirements.

Compositions which can be cured to form siloxane elastomers, which contain a highly viscous polydiorganosiloxane, a reinforcing silicon dioxide filler, a copolymer comprising $R_3SiO_{0.5}$ and SiO_2 units, wherein the radical R represents, for example a methyl group, and mica and an organic peroxide, are known from German Offenlegungsschrift 3 722 755. The proportion of elastomer-stabilising silicon dioxide filler is between 5 and 75 parts by weight for 100 parts by weight of polydiorganosiloxane. The mica proportion, which should effect an improvement in the integrity of the insulation under fire conditions, lies between 85 and 100 parts by weight for 100 parts by weight of polydiorganosiloxane. Too high quantities of mica, for example over 220 parts by weight, lead on the other hand to difficulties during processing and to poorer mechanical properties of the cured elastomer.

German Offenlegungsschrift 3 008 084 describes compositions having up to 300 parts by weight of a

ceramic-forming filler for up to 700 parts by weight of polyorganosiloxane. In order to guarantee adequate elasticity and bendability of the product after crosslinking the mixture, the filler content should however not exceed 100 parts by weight.

United States application 4 288 360 and United States application 3 862 082 contain flame-resistant compositions based on polyorganosiloxanes, which can be cured to form silicone rubbers, having inorganic, for example oxidic fillers, such as titanium dioxide, which function as reinforcing materials. The maximum achievable filler concentrations still do not facilitate on the one hand adequate functional property under extreme conditions, on the other hand the resulting filled polyorganosiloxane compositions still do not have satisfactory mechanical properties for handling under normal conditions.

Mica bands applied directly to the conductor wire find the largest area of application, particularly for high requirements in terms of fire technology. For the functional property according to E 90, hitherto only cables of this type are thus used, wherein the mica band are used mostly in conjunction with the highly filled polymers described above or with other additional ceramic materials. Hence German Offenlegungsschrift 4 132 390 describes electrical cables with functional property, in which to insulate the individual conductors an insulating layer is provided which consists of two layers of a glass-fabric band coated with mica and a thin layer of a high temperature-resistant ceramic adhesive arranged therebetween. United States application 5 227 586 likewise contains flame-resistant electrical cables which are resistant to temperatures of 1,000°C, in which the electrical conductors surrounded by an insulating

material, such as silicone rubber, are situated in a sleeve made of two flame barrier layers applied one over another, for example mica layers. Swiss application 683 213 also describes electrical cables with insulation and/or functional property, in which the individual wires are surrounded by a first bandage consisting essentially of glass-fibre tape and mica platelets. This bandage is provided with insulation made from halogen-free polymer, which is finally surrounded by a second bandage made from glass yarn.

A considerable disadvantage in using mica bandages in fire-proof cables is based in the high costs associated therewith. Furthermore, mica bandages on electrical conductors also have only limited temperature resistance and only limited stability with respect to mechanical stresses. Specially suitable types of mica and increasing layer thicknesses therefore have to be used with increasing requirements. A further disadvantage consists in using resins and binders between mica particles and glass-fabric supports intended for fixing which are mainly not highly temperature resistant. Many other ceramic materials also often do not have the required adequate electrical dielectric strength over the temperature range and likewise do not form an economical alternative due to high costs. For the said reasons there is a considerable need for further materials or material compositions which permit the manufacture of fire-proof cables which satisfy high safety requirements at an acceptable price. In addition, the diverse bands in the cable impair handling during cable assembly, namely during peeling off and stripping the cable ends. Expense for cable assembly increases with increasing number of tape lappings.

The object of the present invention is to provide a cost-effective material which can be used at

lower layer thickness compared to the above-mentioned materials and hence with improved efficiency, and which is to be processed without difficulty and is particularly suitable for manufacturing electrical cables with high insulation and/or functional properties, but also facilitates applications in excellent manner in preventative fire protection generally, as for fire-protective casings. The material should also have excellent mechanical properties even at conventional use temperatures.

This object was achieved by a composition according to claim 1, a ceramisable flame-resistant composition containing at least one organosilicon polymer, at least one ceramisable filler and at least one melting and resolidifying or melting and ceramising or melting and crystallising, mineral component, which melts at a lower temperature compared to the sintering temperature of the ceramisable filler, and optionally further auxiliaries and additives (claim 1).

The object of the invention is also electrical wires or cables having insulating and/or functional properties, but also applications in preventative fire protection generally, such as fire-protective casings, distributor boxes or coupling sleeves, which contain at least one constituent based on this ceramisable composition.

The invention is based on the knowledge that in known compositions in the event of fire a critical temperature range was often observed between the destabilising decomposition of the organosilicon polymer structure and stabilising sintering processes of the filler components, during which there is no optimum protection. This temperature range is minimised by the composition of the invention.

The high mechanical strength of the flame-resistant compositions, which is responsible for adequately high insulating and/or functional properties in the event of fire, is achieved according to the proven principle of a compound provided with wetting agent. The silicon dioxide (SiO_2) present when combusting the organosilicon polymer or freely in the compound reacts with the ceramising filler(s) in a sintering reaction which proceeds, according to electron microscope investigations, in the form of edge layer sintering of the substances normally existing in powder form. The critical temperature range described above between the destabilising decomposition of the organosilicon polymer structure and the onset of first stabilising sintering and ceramising processes, during which maximum stability of the composition is not achieved, may be significantly reduced according to the invention by the novel addition of at least one melting and resolidifying or ceramising or crystallising, mineral component having a lower melting point compared to the sintering temperature of the ceramising filler, for example a so-called "glass" or a "clay". The functional principle is based on displacement of the reaction and solidification mechanism to lower temperatures, which depends on the softening point of the glass or clay component. An increase in plasticity and improvement in crack formation or crack advancing behaviour is associated therewith. The flame-resistant properties in the critical temperature ranges described above may also be further improved particularly by suitable selection of two or more "glasses" and/or "clays".

A "glass" is understood in the sense of the present invention to mean a melt solidified without crystallisation, the atoms of which indeed have a short-range order but not aligned long-range order. It is usually formed when the rate of "crystal nucleation" in a

melt below its melting point is low compared to the cooling rate of the molten material.

In a preferred embodiment, the composition of the invention contains a wetting agent for the ceramising filler (claim 2). The flame-resistant composition thus has at least one wetting agent for the ceramising fillers, wherein in particular surfactants, natural or synthetic amphiphilic chemical substances, are used.

In a further preferred embodiment, the component(s) (for example the glass/glasses) is (are) incorporated into the composition as distributed granular particles (claim 3).

In a further preferred embodiment of the present invention, a (such) component(s) (such as for example glass/glasses) is (are) used which have a melting point of 900°C at the most (claim 4). These components are particularly preferred when they have a melting point between 400°C and 800°C, a (such) glass/glasses having (a) melting point(s) between 400 and 700°C is (are) most particularly preferred.

For example mixtures of acidic oxides (silicon dioxide, boron trioxide, aluminium trioxide, inter alia, which form a three-dimensional network, with basic oxides (sodium, potassium, magnesium, lead, calcium, zinc oxide or others) show the property of glassy solidification from the melt fusion. The main constituent of such glasses is silicon dioxide. The siloxane bridges are partially cleaved by adding the basic metal oxides or the corresponding monovalent or divalent cations. The more separating sites of this type which are available, the lower the softening or melting point of the glass. However, silicon may also be partly replaced by other network-forming ions (for example trivalent boron or

aluminium or pentavalent phosphorus). They are then the so-called "silicate glasses".

Enamel and glass frits, glass solders, composite and lead glasses, crystallising glasses may be mentioned as suitable examples of glasses of the invention, as are generally commercially available. If required, so-called crystallising glasses are also used which are characterised by renewed solidification from the melt phases at high temperatures.

Fire-inhibiting glass frit, for example in powder form, is preferably used as the glass component. Particularly preferred are thus those glass frits which melt continuously over a temperature range from 350 to 900°C, so that the base material is systematically enclosed and thus protected against fire. Such particularly preferred glass frits typically have a refractive index between 1.4 and 1.7, in particular between 1.5 and 1.6. Their average particle size is between 2 and 70 μm , in particular between 2 and 50 μm . They typically have a specific surface area of 0.5 to 2 mm^2/g . At high temperatures (about 1,000°C) the glass frits then typically form a sealed, crystalline-glassy barrier to smoke, poisonous fumes and flames. Temperatures of up to 1,100°C may be tolerated without the material of the invention itself developing smoke or poisonous fumes.

In a preferred embodiment of the present invention, a mixture of glass frits and low-alkali glasses having a melting point of less than 750°C is used as the low-melting glass component (claim 5). Mixtures of lead-free and low-alkali glasses with glass frit typically have a higher melting point than the glass frits alone, which often melts even at temperatures below 500°C. At the same

time the high alkali content, optionally also the high lead oxide content, of the glass frit, which is disadvantageous for the electrical insulating properties of the composition of the invention used, for example in the insulating layer of fire-proof cables, may be reduced by admixing the lower-alkali glass. The glass frit used is thus present particularly as a frit powder. The frit powder for the mixture has a density between 2.5 and 3.0 g/cm³ and an average grain diameter of about 50 μ m.

Glass solders serve for producing rigid, usually electrically insulating and hermetic bonds between materials, such as glass, ceramic or metal. Analogously to metallic solders the habit has been to designate only special glasses having a particularly low melting temperature as glass solders, by means of which the said bonds may be produced, in contrast to fusible glasses, with a minimum temperature load.

Glass solder bonds are produced - depending on the geometrical degree of difficulty of the bond - in the viscosity range from 10^4 to 10^6 dPas. Glass solders reach these viscosity values depending on thermal expansion in the temperature range from about 400 to 700°C. The transformation temperature T_g of the glass solders, that is the temperature at which a drastic change in thermal expansion of the glass takes place (transition of the glass from the rigid solid state to the state of sub-cooled liquid), lies in the temperature range from about 300 to 500°C. Stable glass solders, crystallising glass solders and composite glass solders are differentiated according to their behaviour during the soldering process. A particularly preferred composite glass solder having a lead oxide content of less than 5 wt.% and an alkali content in the ppm range has a glass transition

point of 490 to 560°C, a softening point from 590 to 660°C and an average particle size between 5 and 15 μm . The lowest glass transition temperatures T_g and hence also soldering temperatures are achieved using lead oxide-containing glasses, for example lead borate glasses. In this way soldering temperatures from about 400°C are possible. Largely lead oxide-free glass solders melt on the other hand only at temperatures from just under 700°C.

Stable glass solders behave like normal glasses. Their properties do not change during the soldering process. In the case of reheating the soldering point, their softening shows the same temperature dependence as for the preceding soldering process. On the other hand, crystallising glass solders have an increased tendency to crystallisation. They convert into a ceramic-like, polycrystalline state during the soldering process. A more pronounced thermal re-loading of the solder compound is thus possible. Remelting of the crystals only sets in at a more marked temperature increase above the soldering temperature.

The two terms glass solders and passivating glass relate primarily to the different use of the particular types of glass. Hence they are application-oriented terms. Glass solder is used for fixing of glass, ceramic or metal, passivating glass on the other hand for surface protection of semi-conductor components. In a comparison of the types of glass used in each case for these two areas of application, the glass solders usually melt at lower temperatures than the passivating glasses.

The molten glass layers of passivating glasses offer safe protection from mechanical and/or chemical effects. The passivating glasses are typically zinc borate or zinc borosilicate glasses or lead silicate or lead

borosilicate glasses having a low proportion of alkali metal oxide concentrations. In a preferred embodiment of the present invention, a composition is claimed which has at least one crystallising passivating glass having an alkali metal oxide proportion of less than 600 ppm as the low-melting glaze component (claim 6). Low lead oxide zinc borate or zinc borosilicate glasses are thus particularly preferred. They have glass transition temperatures between 510 and 570°C, softening temperatures between 590 and 660°C and melting points between 650 and 710°C. Crystallising zinc borate glasses having a low lead oxide portion are most particularly preferred. This lead oxide portion typically lies below 5 wt.%, wherein the lead oxide is bound into the glass structure essentially as solid. More than 20 wt.% ZnO and B₂O₃ and more than 5 wt.% SiO₂ are given as main constituents of the zinc borate glasses. The passivating glasses are characterised by an extremely low proportion of effective alkali metal oxide concentrations. This proportion preferably lies at less than 600 ppm, most particularly preferably are less than 200 ppm Na₂O, less than 200 ppm K₂O and less than 50 ppm Li₂O. The passivating glass exists typically in a grain size of 99 % < 40 μm and about 50 % < 8 μm. The density of the passivating glass is preferably between 3.4 and 3.9 g/cm³.

Ceramic surfaces may be provided with glassy coatings known from the very different use and practical applications with the aid of glazes. Depending on the type of fluxing agent, melt phases PbO and/or B₂O₃-containing glazes may occur from 500°C. "Glaze" is defined according to application. Ceramic particles may be dissolved and joined to one another in the melt phase by means of a glaze. The fact underlying this effect is that glazes are fundamentally richer in fluxing agent than the

"pieces", which is why they have a dissolving effect on the ceramic surface. Filler grain binding may thus be achieved by dissolving the ceramic particle surface in the melt phase.

The particles incorporated into the compounds, particularly particles of materials described above, melt under the action of heat, for example due to a case of fire, even at low temperatures (depending on type even at 400°C). The molten phase diffuses into the bordering regions of the grain structure consisting mainly of metal oxide fillers. The grain structures in turn favour this diffusion process due to the formation of a capillary effect. Hence in the event of fire large vitrified regions are produced in good time at low temperatures in the compounds which in volume are considerably greater than the former particles themselves. In some cases cavities may even occur - caused by complete melt diffusion - at the original location of the particles which are however not a negative impairment due to their complete inclusion in the glass phase. At the same time the liquid glass phases between the grain structures of the fillers and the pulverulent degradation products of the organosilicon polymer already present to a different extent, facilitate a type of plastic behaviour. Tensions from the loading mechanism are thus partly effectively caught by deformation or flowing. In addition, the solidifying influence exerted by the glass phase may be assisted as a function of the glass/glaze and metal oxide type by dissolving the grain surface of the metal oxides in the glass (glaze) component. The viscosity of the melt is thus increased, which contributes overall to a considerably lower sensitivity of the system, inter alia, to dripping, and due to low-viscosity melt fusion, freely moving charge carriers.

In order to guarantee the required electrical insulating properties of the flame-resistant compositions, the composition of the invention should be free of or low in electrically conducting components, such as for example ions. Particularly in the molten state, a minimum concentration of such components is an important characteristic. Therefore in the composition of the invention such glasses/glazes are preferred, the proportion of electrically conducting inclusion materials of which, that is particularly ions, is as low as possible. The intended application should thus also always be taken into account. A recipe for application in a fire alarm cable, which is tested at a voltage of 110 V, may have a higher proportion of conductive constituents than a low voltage cable which is tested at 380 V.

In a further preferred embodiment, there are at least 1.0 parts by weight of the glass (glasses) or the glaze(s) per 100 parts by weight of organosilicon polymer(s). Compositions having 1 to 70 parts by weight of the glass (glasses) or glaze(s) are particularly preferred (claim 7). Most particularly preferred are those compositions, the proportion of glass or glaze component(s) of which is between 10 and 60 parts by weight per 100 parts by weight of the organosilicon polymer(s). Compositions having 20 to 50 parts by weight of the glass or glaze component(s) per 100 parts by weight of the organosilicon polymer(s) are particularly preferred.

The proportion of glass (glasses) or glaze(s) used in the flame-resistant compounds may thus depend considerably on the type and the concentration of ceramising filler, wherein the particular property required (for example the strength as mechanical property) which applies to optimise it for the particular application, is thus always taken into account. Tables 1 and 2 provide an incomplete

overview of properties of compositions having certain filler proportions, certain proportions of a glass or glaze component (a combination of two or more glass or glaze components always being possible), also as a function of the type of glass or glaze component. Summarising it should be stated that the particular intended application determines the selection of the glass or glaze component or its concentration in the composition.

Electron microscope images also show a positive influence of the glass inclusions on crack formation within the compound due to increased mechanical stress. Hence the tendency to crack formation is above all considerably reduced in combination with such materials which have a significantly higher thermal expansion coefficient, for example metals, such as copper wire. Energy is withdrawn from the crack when a crack occurring nevertheless passes through a glazed area. This dissipation of crack energy leads to crack aversion, crack branching or to cessation of crack progress. In some cases cracks running together could be properly blocked by a glass inclusion and hence its contact and surface-area expansion properly prevented. Hence complete separation of the ceramic layer is prevented or delayed. Increased breaking strength in the compound of the invention, increased boundary surface bonding to copper (wire) and improved bonding by mutual infiltration in the boundary surface region associated with lower material shrinkage, goes along with this. In addition, the composition of the invention does not have unfavourable properties as regards plasticity, crosslinking (vulcanisation), expansion after crosslinking and crack susceptibility compared to compounds without added low-melting glass (glasses) or glaze(s) in normal use, that is at room and use temperature (for example to 90°C).

However, clays (for example kaolinite, illite) may also be incorporated in the composition as the low-melting and ceramising component instead of or together with the glasses. For example during thermolysis of kaolinite, hydroxidically bound water is initially released, then silicon dioxide, corundum and amorphous flake-like mullite is produced with volume reduction and pore formation. A melt phase in which amorphous silicon dioxide and amorphous mullite dissolve is formed about 950°C by liquifying the feldspar. Furthermore, potassium oxide (for example from feldspar or illite) and silicon dioxide form a glass which can cement smaller ceramic particles after cooling the ceramic product.

The polymers which are known in this field, commercially available, preferably elastic or elastifiable, such as polyorganosilazanes, polyorganosiloxanes (silicones), for example silicone resins, silicone gums and silicone rubbers, such as HTV silicone rubber, are advantageously used as organosilicon polymers. Polyorganosiloxanes (silicones) are thus preferably used. The organosilicon polymers may be present alone or in mixtures and their free content of silicon dioxide (SiO_2) may vary, but are in preferred manner the matrix for the ceramising fillers. Organosilicon polymers having an average silicon dioxide content, as exists in HTV silicone rubbers having a Shore A hardness of 40-80, are preferably used. Polyorganosiloxanes (silicones) having low or average viscosities are particularly suitable, since they permit a high content of ceramising, or optionally also non-ceramising fillers. However, highly viscous polymers having a lower maximum content of ceramising fillers are also used, for example in constituents of fire-proof cables having less stringent safety requirements. The group of generally suitable organosilicon polymers includes both molecules having functional groups suitable for crosslinking, such as for example hydroxyl or vinyl

functions, and those without crosslinkable functions; the composition of the invention may be present both in the initial state and in the finally processed end product in non-crosslinked, crosslinked or partially crosslinked form. The form of the composition thus also depends on the required filler concentration inasmuch as the crosslinking density is reduced with increasing filler concentration towards quasi thermoplastic characteristics, whereas for lower concentrations at least partial crosslinking is present.

All compounds forming ceramic with silicon dioxide are suitable as ceramising fillers, for example silicates, such as aluminium silicate, titanium silicate and magnesium silicate, aluminates, such as sodium aluminate, nitrides, such as silicon nitride, boron nitride and aluminium nitride, carbides, such as tungsten carbide, titanium carbide and molybdenum carbide.

In a preferred embodiment, oxides, such as magnesium oxide, titanium dioxide and in particular aluminium oxide (claim 8) or mixed oxides preferably, in particular mixed oxides of Al_2O_3 and SiO_2 , for example mullite ($3 \text{ Al}_2\text{O}_3 \times 2 \text{ SiO}_2$), are used. The ceramising fillers may be used both in the pure form of the above-mentioned substances and in mixtures thereof, oxides preferably being used in principle. Preference is given to the use of aluminium oxide in all its existing modifications, for example $\alpha\text{-Al}_2\text{O}_3$. Also falling under the term ceramising fillers are their precursor compounds, that is substances which convert to the fillers described above, for example under the action of heat. Hence instead of aluminium oxide, the different modifications of aluminium hydroxide, such as bayerite, hydrargillite, boehmite and diaspore, may also be used which convert to aluminium oxide during heating. However, the ceramising substances as such are preferably used.

The ceramising filler is advantageously present in finely powdered form having a specific surface area of about 0.5-10.0 m²/g, preferably 1.0-5.0 m²/g, and an average grain size of about 0.5-4.0 μm, preferably 1.5-2.5 μm. The quantity of the filler is selected according to the intended use and the requirements of functional property. The composition advantageously contains at least 50 parts by weight (claim 9), particularly preferably at least 100 parts by weight, and most particularly preferably at least 200 to 300 parts by weight of ceramising filler, for 100 parts by weight of organosilicon polymer(s). The upper limit of the filler concentration is determined by the practical conditions, hence also by selection of the organosilicon polymer(s), and is about 450 to 500 parts by weight per 100 parts by weight of organosilicon polymer(s). Suitable filler concentrations lie advantageously in the range from 100 to 500 parts by weight, for higher requirements from 200 to 500 parts by weight, and preferably from 250 to 400 parts by weight, per 100 parts by weight of organosilicon polymer(s). A high mineral filler proportion is generally preferred.

Advantageous wetting agents are metal soaps in a preferred embodiment; aluminium soaps are thus particularly preferred (claim 10). The metal soaps as are generally conventionally available in commerce, for example having melting ranges from 100 to 150°C, are in particular salts of higher fatty acids. Aluminium stearate is particularly preferably used. The metal soaps may additionally also be used in crude form having a greater or lesser degree of free fatty acids.

The proportion of wetting agent depends on the concentration of ceramising filler and is advantageously at least 0.5 parts by weight per 100 parts by weight of organosilicon polymer(s), and advantageously at least

3 parts by weight. Advantageous quantities of wetting agent lie in the range from 0.5 and 25, in particular from 1 to 20, for example from 3 to 15 parts by weight per 100 parts by weight of organosilicon polymer(s).

In a preferred embodiment, the flame-resistant composition has one or more auxiliaries and/or additives. These auxiliaries and additives particularly include additional non-ceramising fillers and crosslinking agents (claim 11). Particularly preferred non-ceramising inorganic fillers are thus carbonates, in particular calcium carbonate (CaCO_3) or magnesium carbonate (MgCO_3) (claim 12), mixtures of calcium and magnesium carbonate or mixed salts thereof, such as Mg-Ca carbonate hydrates, which are also used in conjunction with traditional, already known polymer compounds. Calcium carbonate is thus most particularly preferably used. The proportion of non-ceramising fillers is advantageously up to 200 parts by weight, preferably up to 150 parts by weight, for example 10-100 parts by weight of filler per 100 parts by weight of organosilicon polymer(s). The practical upper limit for the total sum of ceramising and non-ceramising fillers in the composition of the invention is thus, as described above, about 450 to 500 parts by weight per 100 parts by weight of organosilicon polymer(s).

The composition of the invention may optionally contain further auxiliaries and additives, in particular processing aids, plasticisers, crosslinking catalysts or crosslinking agents and pigments.

Depending on the type of organosilicon polymer(s), the composition may also contain conventional, commercially available crosslinking agents. In a preferred embodiment organic peroxides (claim 13), such as correspond to the state of the art for crosslinking of silicones,

preferably benzoyl peroxide, 2,4-dichlorobenzoyl peroxide, dicumyl peroxide or 2,5-dimethyl-2,5-di[t-butylperoxy]hexane, or crosslinking catalysts, for example addition catalysts, such as finely divided platinum or platinum compounds, are used. The quantity of crosslinking agent(s) in the composition is, if required, advantageously up to 5 parts by weight, for example 0.5 to 5 parts by weight, preferably 1 to 3 parts by weight, per 100 parts by weight of organosilicon polymer(s).

The composition of the invention having at least one organosilicon polymer, at least one ceramisable filler, at least one wetting agent for the ceramising filler and at least one melting and resolidifying or crystallising or ceramising glass/glaze or clay, is preferably present as a so-called ceramic polymer compound, that is as a processable mixture, but may also be a - for example non-crosslinked - precursor of such a compound.

In a preferred embodiment, the composition of the invention contains mineral fibres, particularly silicate, glass or ceramic fibres (claim 14). These non-combustible mineral fibres may form a laminate structure either as a fabric together with the compound or exists randomly in the compound.

The composition of the invention may be produced and processed according to the processes also known in the state of the art for other highly filled mixtures by mixing or compounding, that is incorporating the glass/glaze together with the ceramising filler into the conventional constituents, for example using conventional kneading machines or on traditional rubber rolling mills (claim 15). Conventional processing methods, such as extrusion or coextrusion, are also very possible taking

into account special factors, for example an increased abrasive behaviour of the compound.

The conventional crosslinking agents, for example organic peroxides, are optionally added to the composition in the course of compounding. Crosslinking of the polymer matrix takes place according to known methods, advantageously after shaping at elevated temperature. However, crosslinking may also take place according to other mechanisms in the presence of suitable functional groups, for example via a hydrosilylation reaction in the presence of suitable addition catalysts.

The composition of the invention having the glass/glaze or clay is preferably used in flame-resistant insulating materials, particularly preferably for fire-proof cables, and here most particularly preferably in the field of wire insulation, common wire covers or windings, separating layers, that is the layers between the conductor and the insulation, intermediate and external sheaths, and accessories. However it is also predestined for use as filling composition or separating layer in coupling sleeves and distributor boxes or for fire-proof casings in the field of preventative fire protection (claim 16).

A further object of the invention is electrical wires or single-wire or multiple-wire electrical cables having insulating and/or functional properties, which contain at least one constituent based on a ceramisable composition having a melting and resolidifying or ceramising or crystallising, mineral component according to one of claims 1 to 14 (claim 17).

In a preferred embodiment, these electrical wires or cables having at least one constituent based on a

ceramisable composition with a glass/glaze are present in combination with a constituent made of silicone rubber (claim 18).

In a further preferred embodiment, the electrical wire or the electrical cable in the constituent which is made on the basis of the ceramisable composition of the invention, additionally contains a mineral fibre and thus is present as a fibre composite (claim 19).

A most particularly preferred embodiment of the electrical wire or the electrical cable is then present when the constituent based on the ceramisable composition of the invention is the separating layer which is applied to the electrical conductor (claim 20).

In a further most particularly preferred embodiment, the separating layer for the electrical wire or cable made on the basis of the ceramisable composition of the invention is provided with an applied insulating layer preferably made of silicon rubber or other halogen-free rubber or plastics, or mixtures based thereon (claim 21).

The cables obtained on the basis of the composition of the invention do not differ from traditional cables in conventional installation and use. Even stripping the conductor is not a problem. The pulverulent ceramising fillers cannot be recognised as such due to their embedding in the polymer matrix. The properties of the polymer determine the characteristics of the cable. Working up of the ceramising fillers in a compound permits processing, as is known using other traditional highly filled materials. The cables have excellent mechanical properties in the event of fire, in particular high extension at break and low crack formation (chipping), both at conventional use temperatures and in

the ceramised state. The polymer compound of the invention is also a cost-effective alternative to the known materials used. In particular the use of expensive materials, such as mica bandages, may be omitted.

The electrical wires and cables of the invention are illustrated in more detail by the figures below:

Figure 1 shows one example for the construction of an electrical wire 5. The wire shown consists of an electrical conductor 1, a separating layer 2 and insulation 3 in combination with a reinforcing fabric or a network 4, wherein either the separating layer 2 or the insulation 3 or both are made from the ceramic polymer compound of the invention.

The separating later 2 applied to the electrical conductor 1 of the wire 5 preferably consists of the composition of the invention. This separating layer 2 may represent the crucial function-retaining layer and at the same time also an insulating layer in the event of fire. The wall thickness of a separating layer depends on the requirements of the functional property and is advantageously at least 0.3 mm, preferably at least 0.4 mm. The actual insulation 3 of the electrical wire 5 and a reinforcing fabric or a network 4 are situated above the separating layer 2, wherein the sequence of insulation 3 and reinforcing fabric or network 4 above the separating layer 2 may also be exchanged. The insulation 3 may consist of all conventional and permissible materials for this, for example of the halogen-free crosslinkable and non-crosslinkable insulating materials known in this field, for example ethylene-propylene-diene terpolymers (EPDM rubbers). The insulation 3 advantageously consists of a silicone rubber, so that the separating layer 2 of ceramic polymer

compound is integrated in insulation made from silicone rubber. However, the insulation 3 itself may also consist of ceramic polymer compound. A further improvement in the functional property is achieved in both cases. The insulation 3 is optionally combined with a reinforcing fabric or network 4, which consists of a non-combustible mineral material, preferably mineral fibres of silicates, glass and ceramic.

Figure 2 shows an example for the construction of a multiple-wire electrical cable 10. The cable 10 comprises electrical wires 11, 12, 13 and 14, a common wire cover or a winding 15 and an external sheath 16, which is applied over the common wire cover 15. At least one constituent of this electrical cable is produced on the basis of the polymer compound of the invention. The electrical wires which may be constructed, for example according to the wires 5 shown in Figure 1, conventionally have a separating layer based on the composition of the invention. In a preferred embodiment, the common wire cover (winding) 15, alone or together with the separating layers of the wires, comprises the ceramic polymer compound of the invention. A winding made from a flame-resistant halogen-free polymer compound is particularly preferably used. The ceramic polymer compound is thus optionally used in combination with a fabric band made of temperature-resistant mineral materials. The external sheath 16 conventionally consists of traditional materials, for example halogen-free filled polymers, but may alternatively likewise be manufactured using the ceramic polymer compound.

Figure 3 shows one example for the construction of a multiple-wire electrical cable 20 having a concentric conductor 29.

The cable shown comprises four wires 21, 22, 23 and 24, which in turn consist of an electrical conductor 25, a separating layer 26 and insulation 27. However, the wires may likewise have a construction according to the wire 5 described in Figure 1. The cable may also have accessories, such as the central accessory 32 shown here. Wires and accessory are surrounded by a common wire cover or a winding 28. A concentric electrical conductor 29, for example a wrapped copper wire or a copper band winding, is situated above the common wire cover (winding) 28. A further separating layer 30, above which a sheath 31 is situated, is applied to this electrical conductor 29.

According to the invention one or more components of an electrical cable of this type are produced using the ceramic polymer compound. In a preferred embodiment, at least one of the separating layers 26 and 30 consists of the ceramic polymer compound of the invention. The separating layer 26 of the electrical wire preferably consists of ceramic polymer compound and is integrated in insulation 27 made from silicone rubber. In a further embodiment, the common wire cover (winding) 28 is produced either alone or together with the accessory 32 based on the ceramic polymer compound. The external sheath 31 conventionally consists of traditional materials, for example halogen-free filled polymers, but may alternatively likewise be produced using the ceramic polymer compound.

The present invention is illustrated in more detail by the following examples:

Preparation of the mixtures:

300 to 350 parts by weight of Al_2O_3 and 3 to 10 parts by weight of molten aluminium stearate were - according to the example - premixed using a laboratory kneader. The particular mixture was then treated with 100 parts by weight of HTV silicone rubber, Shore A hardness 60, optionally with 10 to 30 parts by weight of glass frit or crystallising passivating glass (the case in Examples 1 to 12, on the other hand glass component was not added to the compositions in the comparative examples 1 and 2) and compounded with 1.5 parts by weight of 2,4-dichlorobenzoyl peroxide.

Alternatively however, compounding may also be carried out in a single-stage process. In this case the fillers are weighed and mixed together in a stirring mixer. The silicone rubber is worked on a roller as a "rough sheet" and then the filler mixture is added and then worked in. Compounding thus takes place on a roller.

Both production processes lead to largely identical results. The two-stage production process, which was used in the following examples, does have better test results for the measuring parameters determined at room temperature.

Execution of mechanical investigations:

The compound strands (diameter 2 mm) were investigated for their structural strength by means of the punch pressure test:

The strands are thus heated to temperatures up to 900°C and then cooled again. A critical temperature range thus exists at temperatures up to 500°C . The silicone is already completely combusted at this temperature, however the ceramising or melting reaction has not yet taken

place. The results which reflect the tolerable load in the punch pressure test are shown in Table 1. In addition, the external characteristics of the sample surfaces were also characterised in more detail. To test the mechanical properties, a round sample was placed longitudinally on a steel plate (45x45 mm) and loaded to break using a flat punch made from steel (diameter 12 mm). Evaluation takes place at break or at a diameter reduction for the round sample to 1.0 mm.

The material strands having a diameter of 2 mm $\pm$ 0.1 mm were also used according to the company's internal processes in addition to determine material shrinkage, structural behaviour and the mechanical properties after thermal treatment. For this the matrix component was crosslinked at 150°C and a retention time of about 10-15 minutes in a warming cupboard.

After crosslinking, strands 20 cm in length were cut, their minimum bending diameter was evaluated at room temperature. The measured value is the distance d (in mm) between the parallel sections of a U-shaped semi-circular strand section, at which partial tearing at the tension surface of the strand just takes place. A value of $d = 0$ mm means that the samples can be bent until the two parallel limbs touch without cracking. The particular measured bending diameter is given in Table 2 (Column B) for the compositions shown.

In this test it should be remembered that the crosslinking state of the material over the whole strand length is partly very different and hence certain scattering may occur for repeated execution of the test. On the basis of a subjective impression, the minimum bending diameter appears to facilitate a first statement on material strength in a tear test. The following thus

applies to a first approximation: the lower the minimum bending diameter, the higher the material tensile strength.

The linear shrinkage was determined with the aid of crosslinked strands 20 cm in length. Thermal treatment then took place such that the strands were placed on a fire-resistant plate of an oven. The oven was heated at 50 K/minute to a final temperature of 1,000°C. The retention time was 180 minutes, after which there was free cooling. Material shrinkage was determined by measuring the strands (using the length L) before and after thermal treatment. Shrinkage is thus produced from the following formula

$$100 \% - \frac{L[\text{cm}] - 20}{20} \times 100 \%$$

20 cm

The results for the different compositions with regard to this material property are listed in Table 2 (Column D).

The tearing behaviour of the crosslinked 20 cm long strands was likewise investigated after the thermal treatment described above (Table 2, Column E). The heated and then cooled materials were thus investigated visually and evaluated using a classification between 0 and 5. The crack opening geometry on the surface in conjunction with the visible depth of the crack was essentially used as the criterion.

The following evaluation scheme was established:

- 0: no cracks or flake-like chipping
- 1: very slight cracks or flake-like chipping/ very narrow opening on the surface
- 2: more pronounced cracks or flake-like chipping/ narrow opening on the surface

- 3: severe cracks or flake-like chipping/ wide opening on the surface
- 4: transition cracks or flake-like chipping - V-shaped splintering/very wide openings on the surface
- 5: very severe splintering/complete cross-sectional deformation

In addition, crack formation, that is particularly the type of crack structures in conjunction with the surface condition, was evaluated, wherein likewise the thermal treatment of the strands described above was used.

The following evaluation scheme was used:

- S: flake-like crack structures or chipping
- R: cracks or splintering
- B: locally narrowly defined bulging projections
- B-R: mostly cracking of the material on the head of the bulging projections

The results of the tests with the different compositions are shown in Table 2 (Column F).

The results of the examples show that the structural strength (SF) may be improved by incorporating 30 phr of crystallising passivating glass into the composition. Optimum structural strength is achieved in the case of a filler proportion of 350 phr (Test example 6 in Table 1). A reduction in the proportion of crystallising passivating glass or of filler leads in each case, alone or in combination, to an impairment of structural strength (for example for the compositions 9 and 10 in Table 1). However, significantly improved values for the structural strength are produced compared to the two comparative tests.

A comparable result for structural strength is also observed for the compositions having glass frits as glass components (Test examples 1 and 5 in Table 1).

Compositions having a high proportion of glass component also show no disadvantages during tearing behaviour or crack formation in spite of their increased strength compared to compositions in the comparative tests (Table 2) when testing other mechanical properties. The compositions of test examples 1 (20 phr glass frit) and 6, 7 or 8 (in all cases 30 phr of crystallising passivating glass) are characterised by the best mechanical properties also compared to the compositions in the comparative tests. The proportion of filler remains without greater significance with regard to the results for strength in the course of the manual bending and breaking test, with regard to the tearing behaviour and with regard to the crack formation. On the other hand, for the measure of material shrinkage, the filler proportion is also important for a constant proportion of glass component (for example comparison of compositions 2 and 5 in Table 2). For an equal proportion of glass component, material shrinkage increases with decreasing filler proportion (see for example composition 2 in Table 2).

Cables and wires of the type according to the invention are suitable for increased applications and permit reduced constructional design with at least equal quality. In particular the use of the teaching of the invention in cables with the aim of functional property in the event of fire leads to it being possible to reduce the function-giving layer thickness when using the compound of the invention having a low-melting component by about 50 % compared to the compounds from the state of the art, that is without the low-melting component. This has considerable advantages in terms of apparatus, namely thinner cables and improved handling, with the same quality and reduces the production costs.

Table 1: Structural strength in the punch pressure test after thermal treatment at 900°C

Example	Filler Al ₂ O ₃ *	Glass type	Adhesion promoter	Punch pressure load [N]
Number	Quantity [phr]	Quantity [phr]	Quantity [phr]	900°C
1	350	C 20	8	195
2	300	C 30	6	165
3	350	C 10	6	188
4	300	C 10	8	92
5	350	C 30	10	132
6	350	G 30	6	214
7	325	G 30	10	138
8	300	G 30	8	147
9	300	G 10	6	90
10	350	G 10	10	64
11	325	C 10	10	60
12	300	C 30	10	147

Comp. 1	350	-	3	24
Comp. 2	350	-	6	25

* two Al₂O₃ types were used

Note: G: crystallising passivating glass, T_g = 530°C

C: glass frit

Table 2

Crosslinker RT state			State after heating at 1,000°C and slow cooling to RT		
A	B	C	D	E	F
1	appr.11		2.5	0-1	S/ slight in places
2	appr. 5		4.0	0-1	R/very little
3	appr. 6		1.5	1	S
4	appr. 3		5.5	4-5	S/very severe
5	appr.13		2.5	0-1	- (B) / few slight bulges
6	appr. 6		1.5	0	-
7	appr. 6		3.0	0	-
8	appr. 2		5.0	1	S/fine design
9	appr.1, some 0	strong pres- sure up to 3	4.5	2-3	S
10	appr. 7		4.5	1	S/fine design
11	appr.10		3.5	2-3	S/fine design
12	appr.10		2.0	0-1	S/ slight in places
Comp. 1	appr. 6		2.5	4	
Comp. 2	appr. 3		0.5	0	

A: Mix number

B: Minimum bending diameter at tear d (mm)

C: Pressure on internal radius/number of tolerable
changing bends

D: Linear shrinkage (%)

E: Cracking behaviour (scale from 0 to 5)

F: Crack picture on the surface/explanations see text

Patent claims

1. Ceramisable flame-resistant composition containing at least one organosilicon polymer and at least one ceramising filler, characterised in that it additionally contains at least one melting and resolidifying, ceramising or crystallising, mineral component, the melting point of which is lower than the sintering temperature of the ceramising filler.
2. Composition according to claim 1, characterised in that it contains at least one wetting agent for the ceramising filler.
3. Composition according to claim 1 or 2, characterised in that the low-melting and resolidifying, ceramising or crystallising, mineral component(s) is/are incorporated into the composition as distributed granular particles.
4. Composition according to one of the afore-mentioned claims, characterised in that the low-melting and resolidifying, ceramising or crystallising, mineral component(s) has/have a melting point of 900°C at the most.
5. Composition according to one of the afore-mentioned claims, characterised in that a mixture of glass frits and low-alkali glasses having a melting point of less than 750°C is used as the low-melting and resolidifying, ceramising or crystallising, mineral component(s).
6. Composition according to one of the afore-mentioned claims 1 to 4, characterised in that at least one crystallising passivating glass having an alkali metal oxide proportion of less than 600 ppm is used as the low-melting and resolidifying, ceramising or crystallising, mineral component(s).

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7. Composition according to one of the afore-mentioned claims, characterised in that the proportion of low-melting and resolidifying, ceramising or crystallising, mineral component(s) is at least 1.0 parts by weight, preferably 1.0 to 70 parts by weight, per 100 parts by weight of the organosilicon polymer(s).

8. Composition according to one of the afore-mentioned claims, characterised in that the ceramising filler is an oxide, preferably aluminium oxide (Al_2O_3).

9. Composition according to one of the afore-mentioned claims, characterised in that the proportion of ceramising filler in the composition is at least 50 parts by weight per 100 parts by weight of organosilicon polymer(s).

10. Composition according to one of the afore-mentioned claims, characterised in that the wetting agent is a metal soap preferably an aluminium soap.

11. Composition according to one of the afore-mentioned claims, characterised in that it comprises one or more auxiliaries and/or additives, particularly additional non-ceramising fillers and crosslinking agents.

12. Composition according to claim 11, characterised in that the non-ceramising filler is a carbonate, particularly CaCO_3 and/or MgCO_3 .

13. Composition according to claim 11, characterised in that the crosslinking agent is an organic peroxide.

14. Composition according to one of the afore-mentioned claims, characterised in that it comprises mineral fibres, particularly silicate, glass or ceramic fibres.

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15. Process for producing a composition according to one of the afore-mentioned claims, characterised in that the low-melting and resolidifying, ceramising or crystallising, mineral component(s) are incorporated into the conventional constituents together with the ceramising filler, particularly on a rolling mill or a kneading machine or by extrusion.

16. Use of a composition according to one of claims 1 to 14 for manufacturing flame-resistant insulating materials, particularly in fire-proof cables, above all as separating layers, sheaths, common wire covers or windings, insulation or accessories, in coupling sleeves or in distributor boxes.

17. Electrical wire or electrical cable having insulating and/or functional properties, containing at least one constituent based on a ceramisable composition having at least one low-melting and resolidifying, ceramising or crystallising, mineral component according to one of claims 1 to 14.

18. Wire or cable according to claim 17, wherein the constituent based on the ceramisable composition is present in combination with a component made of silicone rubber.

19. Wire or cable according to claim 17 or 18, wherein the constituent based on the ceramisable composition contains a mineral fibre and is present as a fibre composite.

20. Wire or cable according to one of claims 17 to 19, wherein the constituent based on the ceramisable composition is a separating layer applied to the electrical conductor.

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21. Wire or cable according to claim 20, wherein an insulating layer made of silicone rubber, other halogen-free types of rubber, plastics or mixtures based thereon, is applied to the separating layer.



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