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(54) Title: SURFACE-TREATED FILLER, DENTAL COMPOSITION CONTAINING SUCH A FILLER, PROCESS OF PRODUCTION AND USE THEREOF

(57) Abstract: The invention relates to a dental composition comprising curable components and a surface-treated filler comprising filler particles the surface of which has been treated with a surface-treating agent, the surface-treating agent being characterized by the following features: comprising at least one (meth)acrylate moiety, comprising at least one hydrolysable silane moiety, comprising only one urethane moiety, comprising a linear alkylene moiety AM1 connecting the at least one (meth)acrylate moiety to the urethane moiety, comprising a linear alkylene moiety AM2 connecting the at least one hydrolysable silane moiety with the urethane moiety, the linear alkylene moiety AM1 comprising more carbon atoms than the linear alkylene moiety AM2. The invention also relates to a process of producing such a dental composition, the use of the dental composition in a method of restoring a dental tooth and a kit of parts comprising the dental composition.

SURFACE-TREATED FILLER, DENTAL COMPOSITION CONTAINING SUCH A FILLER, PROCESS OF PRODUCTION AND USE THEREOF

Field of the Invention

The invention relates to a surface-treated filler and a dental composition containing such a filler. Described is also a process of producing such a filler and the use of the dental composition for restoring a tooth. The surface-treated filler is in particular useful for producing a flowable or injectable dental composition having a low viscosity at a low shear rate.

Background

Polymerizable dental compositions for restoring a defect tooth are widely known.

The dental compositions typically comprise a resin matrix containing polymerizable components, an initiator system suitable for curing the polymerizable components and a filler system.

For achieving adequate mechanical properties after hardening, it is generally desired to provide a composition with a high filler load.

However, the filler particles often have a rather polar surface, whereas the polymerizable components are rather non-polar. Thus, incorporating a high amount of a polar filler in a rather non-polar resin matrix can become challenging.

For addressing this issue, the filler particles are typically surface treated with a silane component making the filler particles more compatible with the resin matrix.

However, with an increasing filler load, the viscosity or consistency of the polymerizable dental composition typically increases which makes the dental composition more difficult to handle, in particular during the step of expressing the dental composition from a packaging apparatus.

Nevertheless, for certain applications, the practitioner prefers to have a rather low viscosity and easily flowing dental composition available, which however after curing should still show adequate mechanical properties.

In the patent literature various attempts are described in this respect.

US 10,441,512 B2 (Tanaka et al.) describes a dental flowable composite composition including a polymerizable monomer, inorganic particles (A), and inorganic particles (B), wherein the inorganic particles (A) are surface-treated with a compound expressed by a

general formula (1), the inorganic particles (B), where at least one of a group expressed by a general formula (A) and a group expressed by a general formula (B) is present at surfaces of the inorganic particles (B). In the examples as surface-treating agents mainly 3-methacryloyloxypropyltrimethyoxysilane and 8-methacryloyloxyocytyltrimethyoxysilane are used. The composite composition is said to have good polishability, abrasion resistance, formability, handleability and flexural strength.

US 10,975,229 B2 (Fuchigami et al.) relates to a silane coupling agent and a medical and/or dental curable composition comprising the same. The silane coupling agent is said to impart high affinity to a radical polymerizable monomer, thereby imparting high mechanical strength, flexibility and durability when used for a medical and/or dental curable composition, and an inorganic filler surface-treated with the silane coupling agent. The silane coupling agent includes repeating units such as a urethane bond and polyethylene glycol (ether bond) at specific positions.

US 10,561,584 B2 (Kakinuma et al.) describes a dental adhesive agent which includes a polymerizable monomer, first and second inorganic particles which have been subjected to a surface treatment by a chemical compound, respectively, and a third inorganic particle. In the examples as surface-treating agents mainly 3-methacryloyloxypropyltri-methyoxysilane and 8-methacryloyloxyocytyltrimethyoxysilane are used.

US 10,918,578 B2 (Murata et al.) describes a dental curable composition including polymerizable monomers; inorganic particles (A1) and/or inorganic particles (A2); and inorganic particles (B). The inorganic particles (A1) are surface-treated with a compound expressed by a general formula (1). The inorganic particles (A2) are surface-treated with a compound expressed by a general formula (2). The inorganic particles (B) are particles where a group expressed by a general formula (A) is present at surfaces, are particles where a group expressed by a general formula (B) is present at surfaces, and/or are particles surface-treated with a compound expressed by a general formula (3).

US 11,246,808 B2 (Craig et al.) describes dental composition comprising a polymerizable resin comprising one or more ethylenically unsaturated monomers or oligomers and nano-particles. The nanoparticles have a refractive index of at least 1.600 and an average discrete or aggregate particle size of no greater than 100 nm. The dental composition further comprises inorganic metal oxide filler having a discrete or aggregate average particle size of at least 200 nm.

US 9,050,252 B2 (Craig et al.) describes methods of surface-treating inorganic oxide particles, hardenable (e.g. dental) compositions comprising a polymerizable resin

composition and surface treated particles, as well as surface treated (e.g. nanocluster) inorganic oxide particles, and silane surface treatment compounds. In one embodiment, the method comprises forming a surface treatment compound by reacting a first functional group of a (meth)acrylate monomer having a molecular weight of at least 350 g/mole with a second functional group of a silane compound wherein the first and second functional group react to form a covalent bond; and combining the surface treatment compound with inorganic oxide particles.

Various silane-treatment agents are also described in JP 6,904,646 B2, JP 6220723 B2, JP 6,173,254 and JP 2021/155395 A.

Summary of Invention

None of the options outlined in the prior art is fully satisfying for the practitioner.

There is still a need for a curable dental composition which is easy to handle, in particular a dental composition which can easily be applied to the surface of a tooth to be restored.

In particular, there is a need for a dental composition having little structure which typically goes along with a low viscosity at a low shear rate.

Further, after curing the dental composition should still have adequate mechanical properties.

One or more of the above objects are addressed by the invention described in the present text and claims.

According to one aspect the invention relates to a surface-treated filler comprising filler particles the surface of which has been treated with a surface-treating agent, the surface-treating agent being characterized by the following features:

comprising at least one (meth)acrylate moiety,
comprising at least one hydrolysable silane moiety,
comprising only one urethane moiety,
comprising a linear alkylene moiety AM1 connecting the at least one (meth)acrylate moiety to the urethane moiety,
comprising a linear alkylene moiety AM2 connecting the at least one hydrolysable silane moiety with the urethane moiety,

the linear alkylene moiety AM1 comprising more carbon atoms than the linear alkylene moiety AM2.

A further aspect of the invention is directed to a dental composition comprising curable components and the surface-treated filler described in the present text, particularly in an amount of 40 to 80 wt.% with respect to the weight of the dental composition.

Another aspect of the invention is directed to a process for producing a surface-treated filler as described in the present text, the process comprising the steps of

combining the filler particles with the surface-treating agent, optionally using a dispersing liquid,

reacting the surface-treating agent with the filler particles,
removing the optional dispersing liquid,
optionally drying and sieving the surface-treated filler particles.

Yet still a further aspect of the invention is directed to a dental composition for use in a method of restoring a tooth in the mouth of a mammal, the dental composition being as described in the present text, the method comprising the steps of

bringing in contact the dental composition with the surface of the tooth to be restored,
curing the dental composition by applying radiation.

In addition, the invention is directed to the use of a surface-treated filler for reducing the viscosity of a dental composition at a low shear rate, the dental composition comprising curable components and filler in an amount of 40 to 80 wt.% with respect to the weight of the dental composition.

A further embodiment is directed to kit of parts comprising the dental composition described in the present text and the following parts alone or in combination: a dental adhesive; a dental curing light; an application instrument.

Unless defined differently, for this description the following terms shall have the given meaning:

"One part composition" means that all components of the composition are present together during storage and use. That is, the composition to be applied or used is not prepared by mixing different parts of the composition before use. In contrast to one part compositions, those compositions are often referred to as two-part compositions (e.g. being formulated as powder/liquid, liquid/liquid or paste/paste compositions).

"Two component composition" means that the components are provided as a kit of parts or system in parts separated from each other before use. For use, the respective components or parts need to be mixed.

The term "compound" or “component” is a chemical substance which has a certain molecular identity or is made of a mixture of such substances, e.g., polymeric substances.

A “hardenable or curable or polymerizable component” is any component which can be cured or solidified in the presence of a photo-initiator by radiation-induced polymerization. A hardenable component may contain only one, two, three or more polymerizable groups. Typical examples of polymerizable groups include unsaturated carbon groups, such as a vinyl group being present e.g. a (methyl)acrylate group.

As used herein, "(meth)acryl" is a shorthand term referring to "acryl" and/or "methacryl". For example, a "(meth) acryloxy" group is a shorthand term referring to either an acryloxy group (i.e., CH_2=CH-C(O)-O-) and/or a methacryloxy group (i.e., CH_2=C(CH_3)-C(O)-O-).

As used herein, "hardening" or "curing" a composition are used interchangeably and refer to polymerization and/or crosslinking reactions including, for example, photo-polymerization reactions and chemical-polymerization techniques (e. g., ionic reactions or chemical reactions forming radicals effective to polymerize ethylenically unsaturated compounds) involving one or more materials included in the composition.

“Radiation curable” shall mean that the component (or composition, as the case may be) can be cured by applying radiation, preferably electromagnetic radiation with a wavelength in the visible light spectrum under ambient conditions and within a reasonable time frame (e.g., within about 60, 30 or 10 seconds).

By "paste" is meant a soft, viscous mass of solids (i.e., particles) dispersed in a liquid.

A “particle” means a substance being a solid having a shape which can be geometrically determined. The shape can be regular or irregular. Particles can typically be analysed with respect to e.g., particle size and particle size distribution.

The particle size (d50) of a powder can be obtained from the cumulative curve of the grain size distribution. Respective measurements can be done using commercially available granulometers (e.g., Malvern Mastersizer 2000). “D” represents the diameter of powder particles and “50” refers to the volume percentage of the particles. Sometimes, the 50% is also expressed as “0.5”. For example, “(d50) = 1 µm” means that 50% of the particles have a size of 1 µm or less.

The term "primary particle size" refers to the size of a non-associated single particle. X-ray Diffraction (XRD) is typically used to measure the primary particle size using the techniques described herein.

A “nano-sized filler” is a filler, the individual particles thereof have a size in the region of nanometers, e.g., an average particle diameter of less than 100 nm. Useful examples are given in US 6,899,948 (Zhang et al.) and US 6,572,693 (Wu et al).

The measurement of the size of nano-particles is preferably based on a TEM (transmission electron microscopy) method, whereby a population is analyzed to obtain an average particle diameter. A preferred method for measuring the particle diameter can be described as follows:

Samples approximately 80nm thick are placed on 200 mesh copper grids with carbon stabilized formvar substrates (SPI Supplies- a division of Structure Probe, Inc., West Chester, PA). A transmission electron micrograph (TEM) is taken, using JEOL 200CX (JEOL, Ltd. of Akishima, Japan and sold by JEOL USA, Inc.) at 200KV. A population size of about 50-100 particles can be measured and an average diameter is determined.

"Agglomerated" is descriptive of a weak association of particles usually held together by charge or polarity and can be broken down into smaller entities. The specific surface of agglomerated particles does not essentially deviate from the specific surface of the primary particles the agglomerate is made of (cf. DIN 53206; 1972).

Agglomerated fillers are commercially available e.g., from Degussa, Cabot Corp or Wacker under the product designation Aerosil™, CAB-O-SIL™ and HDK™.

"Aggregated," as used herein, is descriptive of a strong association of particles often bound together by, for example, residual chemicals treatment or partially sintering. The specific surface of aggregated particles is typically smaller than the specific surface of the primary particles the aggregate is made of (cf. DIN 53206; 1972).

Further breakdown of the aggregates into smaller entities may occur during a polishing step applied to the surface of a composition containing the aggregated filler but not during dispersing the aggregated particles in a resin.

Aggregated fillers and processes for the production and surface treatment thereof are described e.g., in US 6,730,156 B1 (Windisch et al.) and US 6,730,156 (Windisch et al.).

The term "associated" refers to a grouping of two or more primary particles that are aggregated and/or agglomerated.

Similarly, the term "non-associated" refers to two or more primary particles that are free or substantially free from aggregation and/or agglomeration.

A “non-agglomerated filler” means that the filler particles are present in a resin in a discrete, un-associated (i.e., non-agglomerated and non-aggregated) stage. If desired this can be proven by TEM microscopy.

“Acid-reactive filler or glass” shall mean a filler or glass that chemically reacts in the presence of an acidic component.

“Non acid-reactive filler” shall mean a filler, which does not show a chemical reaction within 6 min at all, if mixed with a (poly)acid or which shows only a reduced (i.e. time-delayed) reaction.

To distinguish an acid-reactive filler from a non acid-reactive filler the following test can or is to be conducted:

A composition is prepared by mixing Part P with Part L in a mass ratio of 3 to 1, wherein:

Part P contains: filler to be analysed: 100 wt.%.

Part L contains: poly (acrylic acid co maleic acid) (Mw: about 18,000 +/- 3,000): 43.6 wt.%, water: 47.2 wt.%, tartaric acid: 9.1 wt.%, benzoic acid: 0.1 wt.%.

The filler is characterized as non-acid reactive, if within 6 min after preparing the above composition the shear stress is less than 50,000 Pa, if determined by conducting an oscillating measurement using a rheometer by applying the following conditions: using an 8 mm plate, 0.75 mm gap, at 28°C, frequency: 1.25 Hz, deformation: 1.75%.

“Cation reduced aluminosilicate glasses” shall mean a glass having a lower content of cations in the surface region of the glass particle compared with the inner region of the glass particle.

These glasses react much slower upon contact with a solution of polyacrylic acid in water as compared to typical acid-reactive fillers. Examples of non acid-reactive fillers include quartz glass. Further examples are given in the text below.

Cation reduction can be achieved by a surface treatment of the glass particles. Suitable surface treatments include, but are not limited to, acid washing (e.g., treatment with a phosphoric acid or with hydrochloric acid), treatment with a phosphate or treatment with a chelating agent such as tartaric acid.

"Dispersed within the resin" means that filler particles are present in the resin as agglomerated or aggregated or discrete (i.e., un-associated, non-agglomerated and non-aggregated) particles.

An “urethane group” is a group having the structure “-NH-CO-O-“.

An “urea group” is a group having the structure “-NH-CO-NH-“.

An “amide group” is a group having the structure “-NH-CO-“.

The term “visible light” is used to refer to light having a wavelength of about 400 to about 800 nanometers (nm).

“Dental article” means an article which is to be used in the dental field, especially as or for producing a dental restoration. A dental article has typically two different surface portions, an outer surface and an inner surface. The outer surface is the surface which is typically not in permanent contact with the surface of a tooth. In contrast thereto, the inner surface is the surface which is used for attaching or fixing the dental article to a tooth. If the dental article has the shape of a dental crown, the inner surface has typically a concave shape, whereas the outer surface has typically a convex shape. A dental article should not contain components which are detrimental to the patient´s health and thus free of hazardous and toxic components being able to migrate out of the dental or orthodontic article.

“Dental restoration” means dental articles which are used for restoring a tooth to be treated. Examples of dental restorations include crowns, bridges, inlays, onlays, veneers, facings, copings, crown and bridged framework, and parts thereof. An "adhesive" or "dental adhesive" refers to a composition used as a pre-treatment on a dental structure (e. g., a tooth) to adhere a "dental material" (e. g., "restorative" an orthodontic appliance (e. g., bracket), or an "orthodontic adhesive") to a dental surface. An "orthodontic adhesive" refers to a composition used to adhere an orthodontic appliance to a dental (e. g., tooth) surface. Generally, the dental surface is pre-treated, e. g., by etching, priming, and/or applying an adhesive to enhance the adhesion of the "orthodontic adhesive" to the dental surface.

A "dental surface" or “tooth surface” refers to the surface of tooth structures (e. g., enamel, dentin, and cementum) and bone. A composition is “essentially or substantially free of” a certain component, if the composition does not contain said component as an essential feature. Thus, said component is not wilfully added to the composition either as such or in combination with other components or ingredient of other components.

A composition being essentially free of a certain component usually contains the component in an amount of less than about 1 wt.% or less than about 0.5 wt.% or less than about 0.1 wt.% or less than about 0.01 wt.% with respect to the whole composition or material. The composition may not contain the said component at all. However, sometimes

the presence of a small amount of the said component is not avoidable e.g., due to impurities contained in the raw materials used.

"Ambient conditions" mean the conditions which the composition described in the present text is usually subjected to during storage and handling. Ambient conditions may, for example, be a pressure of 900 to 1,100 mbar, a temperature of 10 to 40 °C and a relative humidity of 10 to 100 %. In the laboratory ambient conditions are typically adjusted to 20 to 25 °C and 1,000 to 1,025 mbar (at maritime level).

As used herein, "a", "an", "the", "at least one" and "one or more" are used interchangeably. Also herein, the recitations of numerical ranges by endpoints include all numbers subsumed within that range (e.g., 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, 5, etc.).

Adding an "(s)" to a term means that the term should include the singular and plural form. E.g. the term "additive(s)" means one additive and more additives (e.g. 2, 3, 4, etc.).

Unless otherwise indicated, all numbers expressing quantities of ingredients, measurement of physical properties such as described below and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about".

The terms "comprise" or "contain" and variations thereof do not have a limiting meaning where these terms appear in the description and claims. "Consisting essentially of" means that specific further components can be present, namely those which do not materially affect the essential characteristic of the article or composition. "Consisting of" means that no further components should be present. The term "comprise" shall include also the terms "consist essentially of" and "consists of".

A composition is "essentially or substantially free of" a certain component if the composition does not contain said component as an essential feature. Thus, said component is not wilfully added to the composition either as such or in combination with other components or ingredient of other components. A composition being essentially free of a certain component usually does not contain that component at all. However, sometimes the presence of a small amount of the said component is not avoidable e.g., due to impurities contained in the raw materials used.

Detailed Description

It was found that the surface-treated filler described in the present text has a couple of advantageous properties.

The surface-treatment of the filler particles not only makes the filler particles more compatible with the resin matrix of the dental composition, but also influences the rheological properties, in particular the viscosity profile of the dental composition containing these surface-treated filler particles.

The dental composition becomes more flowable and can be dispensed from a syringe-like packaging material more easily.

In particular, the dental composition has a low viscosity at a low shear rate which is an indication of a lack of internal structure, similar to a Newtonian liquid.

Further, it was also found that the dental composition after hardening still has adequate mechanical properties such as flexural strength and flexural modulus.

Without wishing to be bound to a particular theory it is believed that the length of the two alkylene moieties plays a role and that it is important that the lengths of alkylene moiety AM1 is longer than the length of alkylene moiety AM2. Thus, the urethane moiety should be located closer to the hydrolysable silane moiety than to the (meth)acryl moiety.

It is assumed that by choosing the length suggested in the present text, the likelihood of the formation of undesired hydrogen bridges is reduced and the surface-treating agent is more effective in shielding the surface of the treated filler.

According to one aspect, the invention is directed to a surface-treated filler.

The nature and structure of the filler(s) is not particularly limited unless the intended purpose cannot be achieved. Different kinds of fillers can be used.

The dental composition described in the present text may comprise one or more of the filler (F1), filler (F2), filler (F3), filler (F4), filler (F5) or filler (F6).

The dental composition may contain only one kind of filler (F1) or more kinds of filler (F1), e.g., two, three or four different kinds.

The dental composition may contain only one kind of filler (F2) or more kinds of filler (F2), e.g., two, three or four different kinds.

The dental composition may contain only one kind of filler (F3) or more kinds of filler (F3), e.g., two, three or four different kinds.

The dental composition may contain only one kind of filler (F4) or more kinds of filler (F4), e.g., two, three or four different kinds.

The dental composition may contain only one kind of filler (F5) or more kinds of filler (F5), e.g., two, three or four different kinds.

The dental composition may contain only one kind of filler (F6) or more kinds of filler (F6), e.g., two, three or four different kinds.

Overall, the dental composition typically contains filler in the following amounts: at least 40 or 45 or 50 wt.%; utmost 80 or 75 or 70 wt.%; in a range of 40 to 80 or 45 to 75 or 50 to 70 wt.%; with respect to the weight of the dental composition.

Filler (F1) comprises non-aggregated, non-agglomerated nano-sized particles of SiO_2, ZrO_2 and mixtures thereof.

The nano-sized particles are preferably substantially spherical and substantially non-porous.

Filler (F1) can typically be characterized by at least one or all of the following features:

a) specific surface (BET): 50 to 400 or 60 to 300 or 80 to 250 m^2/g;
b) primary particle size: 5 to 30 or 7 to 20 nm;
c) comprising particles of SiO_2, ZrO_2 and mixtures thereof.

Filler (F1) characterized by the features a) and c) is sometimes preferred.

If desired, the specific surface can be determined according to Brunauer, Emmet and Teller (BET) by using a device (Monosorb) available from Quantachrome.

Silica is an example of a preferred nano-sized filler (F1). Although the silica is preferably essentially pure, it may contain small amounts of stabilizing ion such as ammonium and alkaline metal ions.

Zirconia is another preferred nano-sized filler (F1). A useful method of making zirconium oxide is described e.g., in US 6,376,590 B1 (Kolb et al.).

The application discloses zirconia sols comprising an aqueous phase having dispersed therein a plurality of single crystal zirconia particles having an average primary particle size less than 20 nm, preferably ranging from 7 to 20 nm. The zirconia sols are substantially non-associated (i.e., non-aggregated and non-agglomerated).

Non-agglomerated nano-sized silicas are commercially available e.g., from Nalco Chemical Co. (Naperville, Ill.) under the product designation NALCO COLLOIDAL SILICAS e.g., NALCO products #1040, 1042, 1050, 1060, 2327 and 2329. Non-aggregated fillers are used and described e.g. in US 7,393,882 (3M).

Filler (F2) comprises aggregated nano-sized particles.

Filler (F2) can typically be characterized by the following features alone or in combination:

a) specific surface (BET): 30 to 400 or 50 to 400 or 60 to 300 or 80 to 250 m^2/g;
b) primary particle size: 5 to 100 or 10 to 80 or 10 to 50 nm;
c) mean particle size (aggregates): 0.5 to 2 µm;
d) comprising particles of SiO_2, ZrO_2 and mixtures thereof.

Filler (F2) characterized by the features a) and c), or a) and d), or a), c) and d) is sometimes preferred.

According to one embodiment filler (F2) is characterized by a primary particle size in the range of 50 to 100 nm and a specific surface (BET) in the range of 30 to 50 m^2/g.

If desired, the mean particle size can be determined by light scattering using e.g., a Malvern Mastersizer 2000 device available from Malvern Instruments.

Filler (F2) can be produced according to the processes described e.g., in US 6,730,156 B1 (Windisch et al.).

In particular, filler (F2) can be prepared from a suitable sol and one or more oxygen containing heavy metal compound solution(s) precursors which may be salts, sols, solutions, or nano-sized particles; of these, sols are preferred. For purposes of this invention, a sol is defined as a stable dispersion of colloidal solid particles within a liquid. The solid particles are typically denser than the surrounding liquid and small enough so that the dispersion forces are greater than the gravitational force. In addition, the particles are of a size small enough so that they generally do not refract visible light. Judicious choice of the precursor sols leads to desired degree of visual opacity, strength etc. Factors that will guide the choice of the sol depends on the combination of the following properties: a) the mean size of the individual particles, which is preferably less than about 100 nm in diameter, b) the acidity: the pH of the sol should be preferably be below 6 and more preferably below 4, and c) the sol should be free of impurities that cause undue aggregation (during the filler preparation process) of the individual discrete particles, during the subsequent steps such as spray drying or calcining, into larger size particles that cannot be easily dispersed or commuted and hence decrease the translucency and polishability.

If the starting sol is basic, it should be acidified e.g., by addition of nitric or other suitable acid to decrease the pH. However, choosing a basic starting sol is less desirable since it requires an additional step and may lead to the introduction of undesired impurities. Typical

impurities that are preferably avoided are metal salts, particularly salts of alkaline metals e.g., sodium.

The non-heavy metal sol and heavy metal oxide precursors are mixed together preferably at a molar ratio to match the index of refraction of the hardenable resin. This imparts a low and desirable visual opacity. Preferably, the molar ratio ranges of non-heavy metal oxide ("non-HMO") to heavy metal oxide ("HMO"), expressed as non-HMO:HMO is 0.5:1 to 10:1, more preferably 3:1 to 9:1, and most preferable in the range of 4:1 to 7:1.

In a preferred embodiment where the aggregated nano-sized particles contain silica and zirconium containing compounds, the method of preparation starts with a mixture of silica sol and zirconyl acetate, at about a 5.5:1 molar ratio.

Prior to mixing the non-heavy metal oxide sol with the heavy metal oxide precursor, the pH of the non-heavy metal oxide sol is preferably reduced to provide an acidic solution having a pH of 1.5 to 4.0.

The non-heavy metal oxide sol is then slowly mixed with the solution containing the heavy metal oxide precursor and vigorously agitated. Strong agitation is preferably performed throughout the blending process. The solution is then dried to remove the water and other volatile components. Drying can be accomplished in various ways, including for example, tray drying, fluidized bed and spray drying. In the preferred method where zirconyl acetate is used, drying by means of spray drying.

The resulting dried material is preferably made up of small substantially spherical particles as well as broken hollow spheres. These fragments are then batch calcined to further remove residual organics. The removal of the residual organics allows the filler to become more brittle, which results in more efficient particle size reduction. During calcining, the soak temperature is preferably set at 200°C to 800°C, more preferably 300°C to 600°C. Soaking is performed for 0.5 hours to 8 hours, depending on the amount of material being calcined. It is preferred that the soak time of the calcine step be such that a plateaued surface area is obtained. It is preferred that the time and temperature be chosen such that the resulting filler is white in color, free from black, grey, or amber colored particles, as determined by visual inspection.

The calcined material is then preferably milled to a median particle size of less than 5 µm, preferably less than 2 µm (on a volumetric basis), as can be determined by using a Sedigraph 5100 (Micrometrics, Norcross, Ga.). The particle size determination can be performed by first obtaining the specific density of the filler using an Accuracy 1330

Pycometer (Micrometrics, Norcross, Ga.). Milling can be accomplished by various methods including for example, stirred milling, vibratory milling, fluid energy milling, jet milling and ball milling. Ball milling is the preferred method.

The resulting fillers comprise, contain, consist essentially or consist of aggregated nano-sized particles. If desired, this can be proven by transmission electron microscopy (TEM).

Once dispersed in the resin, the filler (F2) remains in an aggregated stage. That is, during the dispersion step the particles do not break up into discrete (i.e. individual) and un-associated (i.e. non-agglomerated, non-aggregated) particles.

Without wishing to be bound to a specific theory, it is believed that filler (F2) contributes to the polishability of the dental composition described in the present text. It was found that the aggregates of the filler (F2) particles can break up during a polishing step contributing to a smooth surface and a lower light scattering compared to a rough surface. From a clinical standpoint of view this typically results in high gloss retention and colour stability.

If present, filler (F2) is typically present in the following amounts: least 30 or 35 or 40 wt.%; utmost 70 or 60 or 50 wt.%; in a range of 30 to 70 or 35 to 60 or 40 to 50 wt.%; with respect to the weight of the dental composition.

Filler (F3) may comprise agglomerated nano-sized particles.

According to one embodiment, filler (F3) can be characterized by the following features alone or in combination:

a) specific surface (BET): 30 to 400 or 50 to 300 or 70 to 250 m^2/g;
b) comprising particles of SiO_2, ZrO_2, Al_2O_3 and mixtures thereof.

If desired, the specific surface can be determined as described above.

Suitable agglomerated nanoparticles include fumed silicas such as products sold under the tradename Aerosil™ e.g., Aerosil OX-130, -150, and -200, Aerosil R8200 available from Degussa AG, (Hanau, Germany), CAB-O-SIL™ M5 available from Cabot Corp (Tuscola, Ill.), and HDK™, e.g., HDK-H 2000, HDK H15; HDK H18, HDK H20 and HDK H30 available from Wacker.

Without wishing to be bound to a specific theory, it is believed that filler (F2) contributes to the rheological behaviour of the dental composition described in the present text.

Using this kind of filler enables one to provide a highly filled dental composition which nevertheless is still mixable using static mixing tips. From a clinical standpoint of view this

typically results in improved handling properties such as easy mixing of the pastes and low extrusion forces from cartridge systems.

If present, filler (F3) is typically present in the following amounts: at least 1 or 3 or 5 wt.%; utmost 20 or 15 or 10 wt.%; in a range of 1 to 20 or 3 to 15 or 5 to 10 wt.%; with respect to the weight of the dental composition.

Filler (F4) comprises non acid-reactive glasses such as lanthanum glass, borosilicate glass, soda glass, barium glass, strontium glass, glass ceramic, aluminosilicate glass, barium boroaluminosilicate glass, strontium boroaluminosilicate glass; silicates such as calcium silicate, zirconium silicate; and metal oxides such as quartz, cristobalite, alumina, titania, silica-titania, silica-titania-barium oxide, silica-zirconia, silica-alumina.

In particular the following glasses were found to be useful: barium glass, strontium glass, aluminosilicate glass, barium boroaluminosilicate glass and strontium boroaluminosilicate glass.

Useful glasses are commercially available e.g., from Schott like GM32087, GM27884, G018-053, G018-308, G018-431 and G018-432.

If desired, filler (F4) can also be characterized by the following features alone or in combination:

a) specific surface (BET): 10 to 50 or 15 to 40 m^2/g;
b) mean particle size: 0.1 to 1 or 0.2 to 0.6 µm.

If present, filler (F4) is typically present in the following amounts: at least 1 or 5 or 10 wt.%; utmost 80 or 70 or 60 wt.%; in a range of 1 to 80 or 5 to 70 or 10 to 60 wt.%; with respect to the weight of the dental composition.

Filler (F5) comprises acid-reactive fillers, in particular acid-reactive glasses.

The acid-reactive fillers may help to adjust the curing behaviour and adhesion of the dental composition by modulating the pH-value during the hardening process.

Acid-reactive fillers can typically be characterized by the following features alone or in combination:

a) Mean particle size: about 3 to about 10 µm;
b) (d10/µm): from 0.5 µm to 3 µm; (d50/µm): from 2 µm to 7 µm; (d90/µm): from 6 µm to 15 µm.

Examples of filler (F5) include metal oxides and hydroxides of e.g., calcium, magnesium or zink, wherein the use of calcium hydroxide is sometimes preferred; and acid-reactive glasses, in particular fluoroaluminosilicate glasses (FAS glass).

The acid-reactive glass can be produced by melting a glass frit containing the respective glass components, crushing and grinding the glass frit until the desired particle size distribution is obtained. Glass components which can be used include Al_2O_3, SiO_2, SrF_2 and AlF_3-hydrate or AlF_3. The milling or grinding of the glass frit can be done e.g., with a ball mill.

The Al/Si ratio of the acid-reactive glass is typically greater than 1/1 with respect to weight. This means that the acid-reactive glass contains more Al than Si. An Al/Si ratio in the range of greater than 1.0 / 1.0 to 1.6 / 1.0 or greater than 1.0 / 1.0 to 1.4 / 1.0 with respect to weight is often preferred.

If present, filler (F5) is typically present in the following amounts: at least 1 or 5 or 10 wt.%; utmost 80 or 70 or 60 wt.%; in a range of 1 to 80 or 5 to 70 or 10 to 60 wt.%; with respect to the weight of the dental composition.

Filler (F6) comprises heavy metal oxide(s) and fluoride(s). Filler (F6) may contribute to increase the radiopacity of the composition.

“Radiopacity” describes the ability of a hardened dental material to be distinguished from tooth structure using standard dental X-ray equipment in the conventional manner. Radiopacity in a dental material is advantageous in certain instances where X-rays are used to diagnose a dental condition. For example, a radiopaque material would allow the detection of secondary caries that may have formed in the tooth tissue surrounding a filling.

Oxides or fluorides of heavy metals having an atomic number greater than 28 can be preferred. The heavy metal oxide or fluoride should be chosen such that undesirable colours or shading are not imparted to the hardened resin in which it is dispersed. For example, iron and cobalt would not be favoured, as they impart dark and contrasting colours to the neutral tooth colour of the dental material. More preferably, the heavy metal oxide or fluoride is an oxide or fluoride of metals having an atomic number greater than 30. Suitable metal oxides are the oxides of yttrium, strontium, barium, zirconium, hafnium, niobium, tantalum, tungsten, bismuth, molybdenum, tin, zinc, lanthanide elements (i.e. elements having atomic numbers ranging from 57 to 71, inclusive), cerium and combinations thereof. Suitable metal fluorides are e.g., yttrium trifluoride and ytterbium trifluoride. Most preferably, the oxides and fluorides of heavy metals having an atomic

number greater than 30, but less than 72 are optionally included in the materials of the invention. Particularly preferred radiopacifying metal oxides include lanthanum oxide, zirconium oxide, yttrium oxide, ytterbium oxide, barium oxide, strontium oxide, cerium oxide, and combinations thereof. The heavy metal oxide particles may be aggregated. If so, it is preferred that the aggregated particles are equal or less than 200 nm in average diameter. Other suitable fillers to increase radiopacity are salts of barium and strontium especially strontium sulphate and barium sulphate.

If present, filler (F6) is typically present in the following amounts: at least 1 or 3 or 5 wt.%; utmost 50 or 40 or 30 wt.%; in a range of 1 to 50 or 3 to 40 or 5 to 30 wt.%; with respect to the weight of the dental composition.

In certain embodiments, the dental composition may comprise a combination of fillers (F1) and (F2), or (F1) and (F3), or (F2) and (F6), or (F1), (F2) and (F6), or (F2), (F3) and (F6), wherein a combination of fillers (F2) and (F6) is sometimes preferred.

The surface treating agent is characterized as follows:

a. comprising at least one (meth)acrylate moiety,
b. comprising at least one hydrolysable silane moiety,
c. comprising only one urethane moiety,
d. comprising a linear alkylene moiety AM1 connecting the at least one (meth)acrylate moiety to the urethane moiety,
e. comprising a linear alkylene moiety AM2 connecting the at least one hydrolysable silane moiety with the urethane moiety,
f. the linear alkylene moiety AM1 comprising more carbon atoms than the linear alkylene moiety AM2.

The surface-treating agent does not comprise polyol moieties (e.g. polyethylene or polypropylene moieties).

Without wishing to be bound to a particular theory, the presence of polyol moieties in combination with urethane moieties may lead to interactions by hydrogen bonds and may generate an undesired internal structure within the composition.

More precisely, the surface-treating agent can be characterized as follows:

a. comprising only one (meth)acrylate moiety,
b. comprising at least one hydrolysable silane moiety,
c. comprising only one urethane moiety,

d. comprising one linear alkylene moiety AM1 connecting the (meth)acrylate moiety to the urethane moiety, the alkylene moiety AM1 comprising 6 to 12 C-atoms,
e. comprising one linear alkylene moiety AM2 connecting the at least one hydrolysable silane moiety with the urethane moiety, the linear alkylene moiety AM2 comprising 1 to 4 C-atoms.

The hydrolysable moiety of the silane moiety is typically selected from

$$-Si(R^2)_o(R^3)_{3-o}$$

with R^1 = H or CH_3; R^2 = independently selected from Cl, Br, O-C_{1-4} alkyl, O-C_{1-4} acyl; R^3 = independently selected from C_{1-4} alkyl; X = O; Y = NH; n = 6-12; m = 1-4; o = 1-3.

Preferred are often tri-alkyloxysilanes, in particular tri-methoxysilane, tri-ethoxysilane, tri-propyloxysilane or tri-butyloxysilane moiety.

Even more precisely, the surface-treating agent can be characterized by the following formula:

$$H_2C=CHR^1\text{-}CO\text{-}O\text{-}(CH_2)_n\text{-}X\text{-}CO\text{-}Y\text{-}(CH_2)_m\text{-}Si(R^2)_o(R^3)_{3-o}$$

with R^1 = H or CH_3; R^2 = independently selected from Cl, Br, O-C_{1-4} alkyl, O-C_{1-4} acyl; R^3 = independently selected from C_{1-4} alkyl; X = O; Y = NH; n = 6-12; m = 1-4; o = 1-3.

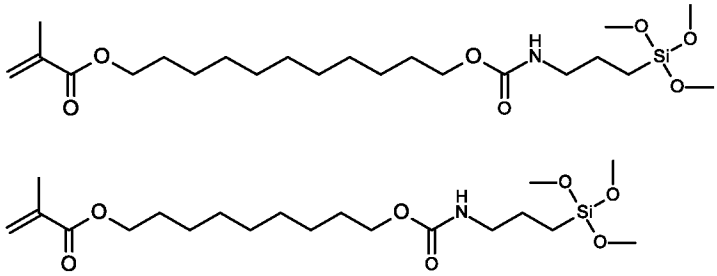
Preferred embodiments of the hydrolysable silane moiety are represented by the following formula:

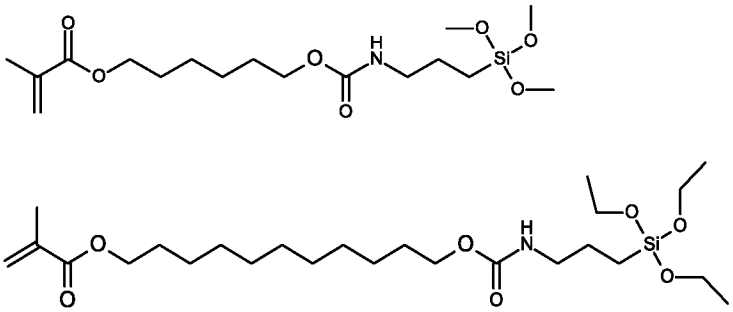
$$H_2C=CHR^1\text{-}CO\text{-}O\text{-}(CH_2)_n\text{-}X\text{-}CO\text{-}Y\text{-}(CH_2)_m\text{-}SiR^2{}_3$$

with R^1 = H or CH_3; R^2 = independently selected from Cl, Br, OCH_3, OCH_2CH_3, $OCH_2CH_2CH_3$, $OCH_2CH_2CH_2CH_3$; X = O; Y = NH; n = 6-12 and m = 1-4.

The surface-treating agent has typically a molecular weight (Mw) in the range of 300 to 800 g/mol or 350 to 600 g/mol.

Particular examples for the surface-treating agent include the following molecules:





The surface-treating agent can be produced by a process comprising the steps of reacting a (meth)acrylate component comprising a hydroxy moiety with a hydrolysable isocyanate silane component.

The reaction is typically done at slightly elevated temperatures (e.g. 40 to 80°C).

The surface-treated filler can be produced by a process comprising the steps

combining the filler particles with the surface-treating agent, optionally using a dispersing liquid,
reacting the surface-treating agent with the filler particles,
removing the optional dispersing liquid,
optionally drying and sieving the surface-treated filler particles.

Suitable dispersing liquids include water and alcohols such as methanol, ethanol or propanol. If desired, the pH value of the dispersion can be adjusted e.g., by adding aqueous ammonia.

In some embodiments, reacting of the surface-treating agent with the filler particles consists of the hydrolysis, i.e. the reaction of water, with at least one of the hydrolysable silane groups, and condensation of resulting silanol groups to the filler surface and/or another surface-treating agent molecule. In some embodiments, the surface-treated filler comprises a partially or fully hydrolyzed surface-treating agent. In some embodiments, the partially or fully hydrolyzed surface-treating agent is fully or partially condensed to form siloxane bonds between adjacent surface-treatment agent molecules, or form siloxane bonds between the surface-treatment agent and the filler surface. In some embodiments, some portion of the hydrolyzed and/or condensed surface-treatment agent can be removed from the surface-treated filler by a re-esterification reaction, i.e. the submersion of the surface treated filler in an alcohol with an effective catalyst to reform the hydrolysable silane moiety. Effective catalysts could include but are not limited to hydrofluoric acid, sodium fluoride, tetramethylammonium fluoride, tetrabutylammonium fluoride, hydrochloric acid, p-toluenesulfonic acid, and trifluoromethanesulfonic acid.

According to another aspect, the invention is directed to a dental composition comprising the surface-treated filler described in the present text.

The dental composition typically comprises a filler system, a resin matrix and an initiator system. The filler system comprises the surface-treated filler described in the present text. The resin matrix comprises the curable components.

The dental composition can typically be characterized by the following properties alone or in combination before hardening:

hardenable within 10 min after irradiation with light having a wavelength in the range of 400 to 700 nm;
pH value: 7 or below.

The dental composition not comprising a rheological modifier typically has a viscosity in the range of 5 to 1,500 Pa*s at 25°C and a shear rate of 0.01 s^{-1};

The dental composition can typically be characterized by the following properties alone or in combination after hardening:

flexural strength: 100 to 200 MPa determined according to ISO 4049 (2019);
flexural modulus: 4 to 8 GPa determined according to ISO 4049 (2019).

If desired, the properties can be determined as described in the example section.

The dental composition comprises curable components.

The curable components are part of the resin matrix. One or more different curable components can be present.

The curable components typically comprise one or more polymerizable moieties, in particular (meth)acrylate moieties. Further, the curable components may comprise acidic moiety(s) or may not comprise acidic moiety(s).

Curable components are typically present in the following amounts: at least 5 or 10 or 15 wt.%; utmost 50 or 45 or 40 wt.%; in the range of 5 to 50; or 10 to 45; or 15 to 40 wt.%; wt.% with respect to the dental composition.

Suitable polymerizable components not comprising acidic moiety(s) which can be used are characterized by the following formula:

$$A_nBA_m$$

with A being an ethylenically unsaturated group, such as a (meth)acryl moiety,

B being selected from (i) linear or branched C_1 to C_{12} alkyl, optionally substituted with other functional groups (e.g. halogenides (including Cl, Br, I), OH or mixtures thereof) (ii) C_6 to C_{12} aryl, optionally substituted with other functional groups (e.g. halogenides, OH or mixtures thereof), or (iii) organic group having 4 to 20 carbon atoms bonded to one another by one or more ether, thioether, ester, thioester, thiocarbonyl, amide, urethane, carbonyl and/or sulfonyl linkages,

m, n being independently selected from 0, 1, 2, 3, 4, 5 or 6 with the proviso that n+m is greater 0, that is that at least one A group is present.

Such polymerizable materials include

mono-, di- or poly-acrylates and methacrylates such as methyl acrylate, methyl methacrylate, ethyl (meth)acrylate, isopropyl (meth)acrylate, n-hexyl (meth)acrylate, stearyl (meth)acrylate, allyl (meth)acrylate, glycerol di(meth)acrylate,

the urethane dimethacrylate called UDMA (mixture of isomers, e.g., Röhm Plex 6661-0) being the reaction product of 2-hydroxyethyl methacrylate (HEMA) and 2,2,4-trimethyl-hexamethylene diisocyanate (TMDI),

glycerol tri(meth)acrylate, ethyleneglycol di(meth)acrylate, diethyleneglycol di(meth)acrylate, triethyleneglycol di(meth)acrylate (TEGDMA), 1,3-propanediol diacrylate, 1,3-propanediol dimethacrylate, 1,6 hexandiol di(meth)acrylate, 1,10 decanediol di(meth)acrylate, 1,12 dodecanediol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, 1,2,4-butanetriol tri(meth)acrylate, 1,4-cyclohexanediol di(meth)-acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, sorbitol hexa(meth)acrylate, bis[1-(2-(meth)acryloxy)]-p-ethoxy-phenyldimethylmethane, and trishydroxyethyl-isocyanurate trimethacrylate;

the bis-acrylates and bis-methacrylates of polyethylene glycols of molecular weight 200 to 500, copolymerizable mixtures of acrylated monomers (see e.g., US 4,652,274 (Boettcher et al.), and acrylated oligomers (see e.g. US 4,642,126 (Zador et al.));

vinyl compounds such as styrene, divinyl succinate, divinyl adipate and divinylphthalate; and

polyfunctional (meth)acrylates comprising urethane, urea or amide groups.

Mixtures of two or more of these free radically polymerizable materials can be used if desired.

If present, the polymerizable component(s) without acidic moiety(s) is typically present in the following amounts: at least 1 wt.% or at least 2 wt.% or at least 5 wt.%; utmost 20 wt.% or utmost 15 wt.% or utmost 10 wt.%; in the range of 1 wt.% to 20 wt.% or 2 wt.% to 15 wt.% or 5 wt.% to 10 wt.%; wt.% with respect to the weight of the dental composition.

The dental composition may also comprise polymerizable monomers with an acidic moiety.

The polymerizable components with an acid moiety can typically be characterized by the following formula

$$A_nBC_m$$

with A being an ethylenically unsaturated group, such as a (meth)acryl moiety,

B being a spacer group, such as (i) linear or branched C_1 to C_{12} alkyl, optionally substituted with other functional groups (e.g. halogenides (including Cl, Br, I), OH or mixtures thereof) (ii) C_6 to C_{12} aryl, optionally substituted with other functional groups (e.g. halogenides, OH or mixtures thereof), (iii) organic group having 4 to 20 carbon atoms bonded to one another by one or more ether, thioether, ester, thioester, thiocarbonyl, amide, urethane, carbonyl and/or sulfonyl linkages, and

C being an acidic group, or precursor of an acidic group such as acid anhydride,

m, n being independently selected from 1, 2, 3, 4, 5 or 6,

wherein the acidic group comprises one or more carboxylic acid residues, such as –COOH or –CO-O-CO–, phosphoric acid residues, such as –O-P(O)(OH)OH, phosphonic acid residues, such as C-P(O)(OH)(OH), sulfonic acid residues, such as –SO_3H or sulfinic acid residues such as –SO_2H.

Examples of polymerizable components with acid moiety include glycerol phosphate mono(meth)acrylate, glycerol phosphate di(meth)acrylate, hydroxyethyl (meth)acrylate (e.g., HEMA) phosphate, bis((meth)acryloxyethyl) phosphate, (meth)acryloxypropyl phosphate, bis((meth)acryloxypropyl) phosphate, bis((meth)acryloxy)propyloxy phosphate, (meth)acryloxyhexyl phosphate, bis((meth)acryloxyhexyl) phosphate, (meth)acryloxyoctyl phosphate, bis((meth)acryloxyoctyl) phosphate, (meth)acryloxydecyl phosphate, bis((meth)acryloxydecyl) phosphate, caprolactone methacrylate phosphate, citric acid di- or tri-methacrylate, poly(meth)acrylated oligomaleic acid, poly(meth)acrylated polymaleic acid, poly(meth)acrylated poly(meth)acrylic acid, poly(meth)acrylated polycarboxyl-polyphosphonic acid, poly(meth)acrylated polychlorophosphoric acid, poly(meth)acrylated polysulfonate, poly(meth)acrylated polyboric acid, and the like. Derivatives of these hardenable components bearing an acid moiety that can readily react e.g., with water to

form the specific examples mentioned above, like acid halides or anhydrides are also contemplated.

Also monomers, oligomers, and polymers of unsaturated carboxylic acids such as (meth)acrylic acids, aromatic (meth)acrylated acids (e.g., methacrylated trimellitic acids), and anhydrides thereof can be used.

Some of these compounds can be obtained, e.g., as reaction products between isocyanatoalkyl (meth)acrylates and carboxylic acids. Additional compounds of this type having both acid-functional and ethylenically unsaturated components are described in US 4,872,936 (Engelbrecht) and US 5,130,347 (Mitra). A wide variety of such compounds containing both the ethylenically unsaturated and acid moieties can be used. If desired, mixtures of such compounds can be used.

Using (meth)acrylate functionalized polyalkenoic acids is often preferred as those components were found to be useful to improve properties like adhesion to hard dental tissue, formation of a homogeneous layer, viscosity, or moisture tolerance.

According to one embodiment, the composition contains (meth)acrylate functionalized polyalkenoic acids, for example, AA:ITA:IEM (copolymer of acrylic acid:itaconic acid with pendent methacrylates).

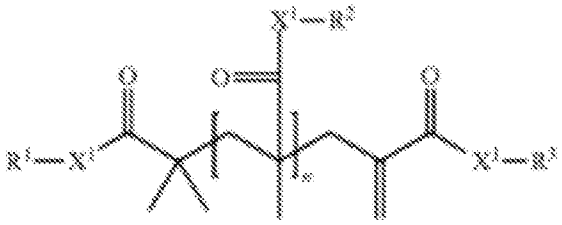
These components can be made by reacting e.g. an AA:ITA copolymer with 2-isocyanatoethyl methacrylate to convert a portion of the acid groups of the copolymer to pendent methacrylate groups. Processes for the production of these components are described, e.g., in Example 11 of US 5,130,347 (Mitra)); and those recited in US 4,259,075 (Yamauchi et al.), US 4,499,251 (Omura et al.), US 4,537,940 (Omura et al.), US 4,539,382 (Omura et al.), US 5,530,038 (Yamamoto et al.), US 6,458,868 (Okada et al.), EP 0 712 622 A1 (Tokuyama Corp.) and EP 1 051 961 A1 (Kuraray Co., Ltd.).

If present, the polymerizable component(s) with acidic moiety(s) should be present in an amount so that the pH value of the composition is below 6, or below 4 or below 2, if brought in contact with water.

If present, the polymerizable component(s) with acidic moiety(s) is typically present in the following amounts: at least 1 wt.% or at least 2 wt.% or at least 5 wt.%; utmost 20 wt.% or utmost 15 wt.% or utmost 10 wt.%; in the range of 1 wt.% to 20 wt.% or 2 wt.% to 15 wt.% or 5 wt.% to 10 wt.%; wt.% with respect to the weight of the dental composition.

If desired, addition fragmentation monomers (AFM) may also be added.

Addition fragmentation monomers can be characterized by the following formula:



wherein

R^1, R^2 and R^3 are each independently Z_m-Q-, a (hetero)alkyl group or a (hetero)aryl group with the proviso that at least one of R^1, R^2 and R^3 is Z_m -Q-; Q is a linking group have a valence of m+1; Z is an ethylenically unsaturated polymerizable group; m is 1 to 6; each X^1 is independently -O- or -NR^4-, where R^4 is H or C_1-C_4 alkyl; and n is 0 or 1.

These monomers are said to lower stress. Suitable monomers are also described in US 9,056,043 (Joly et al.).

Monomers comprising a hydroxyl moiety can also be present.

Suitable compounds include 2-hydroxyethyl (meth)acrylate (HEMA), 2- or 3-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, 5-hydroxypentyl (meth)acrylate, 6-hydroxyhexyl (meth)acrylate, 10-hydroxydecyl (meth)acrylate, dialkylene glycol mono(meth)acrylate, for example, diethylene glycol mono(meth)acrylate, triethylene glycol mono(meth)acrylate, tetraethylene glycol mono(meth)acrylate, polyethylene glycol mono(meth)acrylate, dipropylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, and further 1,2- or 1,3- and 2,3-dihydroxypropyl (meth)acrylate, 2-hydroxypropyl-1,3-di(meth)acrylate, 3-hydroxypropyl-1,2-di(meth)acrylate, N-(meth)acryloyl-1,2-dihydroxypropylamine, N-(meth)acryloyl-1,3-dihydroxypropylamine, adducts of phenol and glycidyl (meth)acrylate, for example, 1-phenoxy-2-hydroxypropyl (meth)acrylate, and 1-naphthoxy-2-hydroxypropyl (meth)acrylate.

If desired, mixtures of one or more of these components can be used.

The dental composition also comprises an initiator system which is suitable for curing the curable components.

The initiator system can be a redox-initiator system, a photo-initiator system or a thermal-curing system. The initiator system is able to start the curing process of the hardenable components being present in the resin matrix.

The initiator system is typically present in the following amounts: at least 0.1 wt.% or at least 0.2 wt.% or at least 0.5 wt.%; utmost 5 wt.% or utmost 4 wt.% or utmost 3 wt.%; in the range of 0.1 wt.% to 5 wt.% or 0.2 wt.% to 4 wt.% or 0.5 wt.% to 3 wt.%; wt.% with respect to the weight of the dental composition.

For curing one-part compositions typically a photo-initiator system is used.

Suitable photo-initiator systems for free radical polymerization are generally known to the person skilled in the art dealing with dental materials.

Suitable photo-initiator systems often contain a sensitizer comprising alpha-alpha di-keto moiety, an anthraquinone moiety, a thioxanthone moiety or benzoin moiety. Sensitizers containing an alpha-alpha di-keto moiety are often preferred.

Typical photo-initiator systems comprise a combination of a sensitizer and a reducing agent or donor component, which is often referred to as photo-initiator system.

As sensitizer, those which can polymerize the polymerizable monomer(s) by the action of a visible light having a wavelength of from 390 nm to 830 nm are preferred.

Examples of sensitizers which can be used include camphor quinone, benzil, diacetyl, benzyl dimethyl ketal, benzyl diethyl ketal, benzyl di(2-methoxyethyl) ketal, 4,4,'-dimethylbenzyl dimethyl ketal, anthraquinone, 1-chloroanthraquinone, 2-chloroanthraquinone, 1,2-benzanthraquinone, 1-hydroxyanthraquinone, 1-methyl-anthraquinone, 2-ethylanthraquinone, 1-bromoanthraquinone, thioxanthone, 2-isopropyl thioxanthone, 2-nitrothioxanthone, 2-methyl thioxanthone, 2,4-dimethyl thioxanthone, 2,4-diethyl thioxanthone, 2,4-diisopropyl thioxanthone, 2- chloro-7-trifluoromethyl thioxanthone, thioxanthone-10,10-dioxide, thioxanthone-10-oxide, benzoin methyl ether, benzoin ethyl ether, isopropyl ether, benzoin isobutyl ether, benzophenone, bis(4-dimethyl-aminophenyl)ketone, 4,4,'-bisdiethylaminobenzophenone.

As the reducing agent or donor component, tertiary amines and the like are generally used. Suitable examples of the tertiary amines include N,N-dimethyl-p-toluidine, N,N-dimethyl-aminoethyl methacrylate, triethanolamine, methyl 4-dimethylaminobenzoate, ethyl 4-dimethylaminobenzoate, methyldiphenylamine and isoamyl 4-dimethylaminobenzoate.

Further suitable reducing agents include diarylalkylamines characterized by the following formula Ar^1Ar^2RN, with Ar^1 and Ar^2 being independently selected from phenyl or alkyl (e.g., C_1 to C_4) substituted phenyl, R being an alkyl (e.g. C_1 to C_4) group wherein one or more H atoms can be substituted by halogen and N being nitrogen. These reducing agents are described in more detail in US 8,314,162 (Hailand et al.).

Moreover, ternary photopolymerization initiating systems consisting of a sensitizer, an electron donor and an onium salt can be used.

Examples are described in US 6,187,833 (Oxman et al.), US 6,025,406 (Oxman et al.), US 6,043,295 (Oxman et al.), US 5,998,495 (Oxman et al.), US 6,084,004 (Weinmann et al.), US 5,545,676 (Palazzotto et al.) and US 8,314,162 B2 (Hailand et al.) and US 6,765,036 (Dede et al.).

In the ternary photo-initiator system, the first component is an onium, preferably an iodonium salt, i.e., a diaryliodonium salt.

The iodonium salt is preferably soluble in the monomer and storage stable (i. e., does not spontaneously promote polymerization) when dissolved therein in the presence of the sensitizer and donor. Accordingly, selection of a particular iodonium salt may depend to some extent upon the particular monomer, polymer or oligomer, sensitizer and donor chosen. Suitable iodonium salts are described e.g. in US 3,729,313 (Smith et al.), US 3,741,769, US 3,808,006 (Smith et al.), US 4,250,053 (Smith et al.) and US 4,394,403 (Smith et al.).

The iodonium salt can be a simple salt (e.g., containing an anion such as Cl^-, Br^-, I^- or $C_4H_5SO_3^-$) or a metal complex salt (e.g., containing SbF_5OH^- or AsF_6^-). Mixtures of iodonium salts can be used if desired. Preferred iodonium salts include diphenyliodonium salts such as diphenyliodonium chloride, diphenyliodonium hexafluorophosphate and diphenyl-iodonium tetrafluoroborate.

The second component in a ternary photo-initiator system is a sensitizer.

The sensitizer desirably is soluble in the monomer and is capable of light absorption within the range of wavelengths of greater than 400 to 1,200 nm, more preferably greater than 400 to 700 nm and most preferably greater than 400 to 600 nm.

Suitable sensitizers can include compounds in the following categories: ketones, coumarin dyes (e.g., ketocoumarins), xanthene dyes, acridine dyes, thiazole dyes, thiazine dyes, oxazine dyes, azine dyes, aminoketone dyes, porphyrins, aromatic polycyclic hydrocarbons, p-substituted aminostyryl ketone compounds, aminotriaryl methanes, merocyanines, squarylium dyes and pyridinium dyes. Ketones (e.g., monoketones or alpha-diketones), ketocoumarins, aminoarylketones and p-substituted aminostyryl ketone compounds are preferred sensitizers.

For example, a preferred class of ketone sensitizers has the formula: $ACO(X)_b B$, where X is CO or $CR^5 R^6$, where R^5 and R^6 can be the same or different, and can be hydrogen, alkyl,

alkaryl or aralkyl, b is zero or one, and A and B different and can be substituted (having one or more non-interfering substituents) can be the same or unsubstituted aryl, alkyl, alkaryl, or aralkyl groups, or together A and B can form a cyclic structure which can be a substituted or unsubstituted cycloaliphatic, aromatic, heteroaromatic or fused aromatic ring.

Suitable ketones of the above formula include monoketones (b=0) such as 2,2-, 4,4- or 2,4-dihydroxybenzophenone, di-2-pyridyl ketone, di-2-furanyl ketone, di-2-thiophenyl ketone, benzoin, fluorenone, chalcone, Michler's ketone, 2-fluoro-9-fluorenone, 2-chlorothioxanthone, acetophenone, benzophenone, 1- or 2-acetonaphthone, 9-acetylanthracene, 2-, 3- or 9-acetylphenanthrene, 4-acetylbiphenyl, propiophenone, n-butyrophenone, valerophenone, 2-, 3- or 4-acetylpyridine, 3-acetylcoumarin and the like. Suitable diketones include aralkyldiketones such as anthraquinone, phenanthrenequinone, o-, m- and p-diacetylbenzene, 1,3-, 1,4-, 1,5-, 1,6-, 1,7- and 1,8-diacetylnaphthalene, 1,5-, 1,8- and 9,10-diacetylanthracene, and the like. Suitable alpha-diketones (b=1 and X=CO) include 2,3-butanedione, 2,3-pentanedione, 2,3-hexanedione, 3,4-hexanedione, 2,3-heptanedione, 3,4-heptanedione, 2,3-octanedione, 4,5-octanedione, benzil, 2,2'- 3 3'- and 4,4'-dihydroxylbenzil, furil, di-3,3'-indolylethanedione, 2,3-bornanedione (camphorquinone), biacetyl, 1,2-cyclohexanedione, 1,2-naphthaquinone and the like.

The third component of a ternary initiator system is a donor.

Preferred donors include, for example, amines (including aminoaldehydes and aminosilanes), amides (including phosphoramides), ethers (including thioethers), ureas (including thioureas), ferrocene, sulfinic acids and their salts, salts of ferrocyanide, ascorbic acid and its salts, dithiocarbamic acid and its salts, salts of xanthates, salts of ethylene diamine tetraacetic acid and salts of tetraphenylboronic acid. The donor can be unsubstituted or substituted with one or more non-interfering substituents. Particularly preferred donors contain an electron donor atom such as a nitrogen, oxygen, phosphorus, or sulfur atom, and an abstractable hydrogen atom bonded to a carbon or silicon atom alpha to the electron donor atom. A wide variety of donors is disclosed in US 5,545,676 (Palazzotto et al.).

Alternatively, free-radical initiators which can be used include the class of acylphosphine oxides and bisacylphosphine oxides.

Suitable acylphosphine oxides can be described by the general formula

$$(R^9)2 — P(=O) — C(=O)—R^{10}$$

wherein each R^9 individually can be a hydrocarbyl group such as alkyl, cycloalkyl, aryl, and aralkyl, any of which can be substituted with a halo-, alkyl- or alkoxy-group, or the two R^9 groups can be joined to form a ring along with the phosphorous atom, and wherein R^{10} is a hydrocarbyl group, an S-, O-, or N-containing five- or six-membered heterocyclic group, or a –Z-C(=O)-P(=O)- $(R^9)_2$ group, wherein Z represents a divalent hydrocarbyl group such as alkylene or phenylene having from 2 to 6 carbon atoms.

Preferred acylphosphine oxides are those in which the R^9 and R^{10} groups are phenyl or lower alkyl- or lower alkoxy-substituted phenyl. By “lower alkyl” and “lower alkoxy” is meant such groups having from 1 to 4 carbon atoms. Examples can also be found e.g. in US 4,737,593.

Examples include bis-(2,6-dichlorobenzoyl)phenylphosphine oxide, bis-(2,6-dichlorobenzoyl)-2,5-dimethylphenylphosphine oxide, bis-(2,6-dichlorobenzoyl)-4-ethoxyphenylphosphine oxide, bis-(2,6-dichlorobenzoyl)-4-biphenylylphosphine oxide, bis-(2,6-dichlorobenzoyl)-4-propylphenylphosphine oxide, bis-(2,6-dichlorobenzoyl)-2-naphthylphosphine oxide, bis-(2,6-dichlorobenzoyl)-1-napthylphosphine oxide, bis-(2,6-dichlorobenzoyl)-4-chlorophenylphosphine oxide, bis-(2,6-dichlorobenzoyl)-2,4-dimethoxyphenylphosphine oxide, bis-(2,6-dichlorobenzoyl)decylphosphine oxide, bis-(2,6-dichlorobenzoyl)-4-octylphenylphosphine oxide, bis-(2,6-dimethoxybenzoyl)-2,5-dimethylphenylphosphine oxide, bis-(2,6-dimethoxybenzoyl)phenylphosphine oxide, bis-(2,4,6-trimethylbenzoyl)-2,5-dimethylphenylphosphine oxide, bis-(2,6-dichloro-3,4,5-trimethoxybenzoyl)-2,5-dimethylphenylphosphine oxide, bis-(2,6-dichloro-3,4,5-trimethoxybenzoyl)-4-ethoxyphenylphosphine oxide, bis-(2-methyl-1-naphthoyl)-2,5-dimethylphenylphosphine oxide, bis-(2-methyl-1-naphthoyl)phenylphosphine oxide, bis-(2-methyl-1-naphthoyl)-4-biphenylylphosphine oxide, bis-(2-methyl-1-naphthoyl)-4-ethoxyphenylphosphine oxide, bis-(2-methyl-1-naphthoyl)-2-naphthylphosphine oxide, bis-(2-methyl-1-naphthoyl)-4-propylphenylphosphine oxide, bis-(2-methyl-1-naphthoyl)-2,5-dimethylphosphine oxide, bis-(2-methoxy-1-naphthoyl)-4-ethoxyphenylphosphine oxide, bis-(2-methoxy-1-naphthoyl)-4-biphenylylphosphine oxide, bis-(2-methoxy-1-naphthoyl)-2-naphthylphosphine oxide and bis-(2-chloro-1-naphthoyl)-2,5-dimethylphenylphosphine oxide.

Tertiary amine reducing agents may be used in combination with an acylphosphine oxide. Illustrative tertiary amines useful in the invention include ethyl 4-(N,N-dimethylamino)benzoate and N,N-dimethylaminoethyl methacrylate.

Commercially-available phosphine oxide photo-initiators capable of free-radical initiation when irradiated at wavelengths of greater than 400 nm to 1,200 nm include a 25:75 mixture, by weight, of bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl phosphine oxide and 2-hydroxy-2-methyl-1-phenylpropan-1-one (formerly known as Irgacure™ 1700, Ciba), 2-benzyl-2-(N,N-dimethylamino)-1-(4-morpholinophenyl)-1-butanone (formerly known as Irgacure™ 369, Ciba), bis(η5-2,4-cyclopentadien-1-yl)-bis(2,6-difluoro-3-(1H-pyrrol-1-yl)phenyl) titanium (formerly known as Irgacure™ 784 DC, Ciba), a 1:1 mixture, by weight, of bis(2,4,6-trimethylbenzoyl)phenyl phosphine oxide and 2-hydroxy-2-methyl-1-phenylpropane-1-one (formerly known as Darocur™ 4265, Ciba), ethyl-2,4,6-trimethylbenzylphenyl phosphine oxide (formerly known as Lucirin™ LR8893X, BASF), and Bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (formerly known as Irgacure™ 819, BASF).

Another free-radical initiator system that can alternatively be used includes the class of ionic dye counterion complex initiators comprising a borate anion and a complementary cationic dye.

Borate salt photo initiators are described, for example, in US 4,772,530 (Gottschalk et al.), US 4,954,414 (Adair et al.), US 4,874,450 (Gottschalk), US 5,055,372 (Shanklin et al), and US 5,057,393 (Shanklin et al.).

Borate anions useful in these photo initiators generally can be of the formula $R^1R^2R^3R^4B^-$, wherein R^1, R^2, R^3, and R^4 independently can be alkyl, aryl, alkaryl, allyl, aralkyl, alkenyl, alkynyl, alicyclic and saturated or unsaturated heterocyclic groups. Preferably, R^2, R^3, and R^4 are aryl groups and more preferably phenyl groups, and R^1 is an alkyl group and more preferably a secondary alkyl group.

Cationic counterions can be cationic dyes, quaternary ammonium groups, transition metal coordination complexes, and the like. Cationic dyes useful as counterions can be cationic methine, polymethine, triarylmethine, indoline, thiazine, xanthene, oxazine or acridine dyes. More specifically, the dyes may be cationic cyanine, carbocyanine, hemicyanine, rhodamine, and azomethine dyes. Specific examples of useful cationic dyes include Methylene Blue, Safranine O, and Malachite Green. Quaternary ammonium groups useful as counterions can be trimethylcetylammonium, cetylpyridinium, and tetramethylammonium. Other organophilic cations can include pyridinium, phosphonium, and sulfonium.

Photosensitive transition metal coordination complexes that may be used include complexes of cobalt, ruthenium, osmium, zinc, iron, and iridium with ligands such as pyridine, 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine, 1,10-phenanthroline, 3,4,7,8-tetramethylphenanthroline, 2,4,6-tri(2-pyridyl-s-triazine) and related ligands.

In a further alternative, heat may be used to initiate the hardening, or polymerization, of free radically active groups.

Examples of heat sources suitable for the dental materials of the invention include inductive, convective, and radiant. Thermal sources should be capable of generating temperatures of at least 40 °C to 15 °C under normal conditions or at elevated pressure.

Thermal curing procedures are sometimes preferred for initiating polymerization of materials occurring outside of the oral environment, e.g., when the composition is used for producing mill blanks or in a postcuring step of an article obtained by processing the composition as resin in an additive-manufacturing method.

The components of the photo-initiator system are typically present in the following amounts: at least 0.1 or 0.2 or 0.3 wt.%; utmost 4 or 3 or 2 wt.%; in the range of 0.1 to 4; or 0.2 to 3; or 0.3 to 2 wt.%; wt.% with respect to the dental composition.

Alternatively or in addition the dental composition can be cured by using a redox-initiator system.

Initiators, which rely upon a redox reaction, are often referred to as "auto-cure catalysts" or "dark cure catalysts". To avoid a premature curing of the dental composition, the two main components of this system (oxidizing and reducing agents) should be kept separate during storage of the dental composition.

As oxidizing components, typically peroxy components such as peroxides are used. Organic peroxides which can be used include di-peroxides and hydroperoxides.

According to one embodiment, the organic peroxide is a di-peroxide, preferably a di-peroxide comprising the moiety R_1-O-O-R_2-O-O-R_3, with R_1 and R_3 being independently selected from H, alkyl (e.g. C_1 to C_6), branched alkyl (e.g. C_1 to C_6), cycloalkyl (e.g. C_5 to C_{10}), alkylaryl (e.g. C_7 to C_{12}) or aryl (e.g. C_6 to C_{10}) and R_2 being selected from alkyl (e.g. (C_1 to C_6) or branched alkyl (e.g. C_1 to C_6).

Examples of suitable organic di-peroxides include 2,2-Di-(tert.-butylperoxy)-butane and 2,5-Dimethyl-2,5-di-(tert-butylperoxy)-hexane and mixtures thereof.

According to another embodiment, the organic peroxide is a hydroperoxide, in particular a hydroperoxide comprising the structural moiety

R-O-O-H

with R being (e.g. C_1 to C_{20}) alkyl, (e.g. C_3 to C_{20}) branched alkyl, (e.g. C_6 to C_{12}) cycloalkyl, (e.g. C_7 to C_{20}), alkylaryl (e.g. C_6 to C_{12}) or aryl (e.g. C_6 to C_{12}).

Examples of suitable organic hydroperoxides include t-butyl hydroperoxide, t-amyl hydroperoxide, p-diisopropylbenzene hydroperoxide, cumene hydroperoxide, pinane hydroperoxide, p-methane hydroperoxide and 1,1,3,3-tetramethylbutyl hydroperoxide and mixtures thereof.

Using hydroperoxides is sometimes preferred, in particular for formulating self-adhesive compositions.

Other peroxides which can be used are ketone peroxide(s), diacyl peroxide(s), dialkyl peroxide(s), peroxyketal(s), peroxyester(s) and peroxydicarbonate(s).

Examples of ketone peroxides include methyl ethyl ketone peroxide, methyl isobutyl ketone peroxide, methyl cyclohexanone peroxide,and cyclohexanone peroxide.

Examples of peroxyesters include alpha-cumylperoxyneodecanoate, t-butyl peroxypivarate, t-butyl peroxyneodecanoate, 2,2,4-trimethylpentylperoxy-2-ethyl hexanoate, t-amylperoxy-2-ethyl hexanoate, t-butylperoxy-2-ethyl hexanoate, di-t-butylperoxy isophthalate, di-t-butylperoxy hexahydroterephthalate, t-butylperoxy-3,3,5-trimethylhexanoate (TBPIN), t-butylperoxy acetate, t-butylperoxy benzoate and t-butylperoxymaleic acid.

Examples of peroxidicarbonates include di-3-methoxy peroxidicarbonate, di-2-ethylhexyl peroxydicarbonate, bis(4-t-butylcyclohexyl)peroxidicarbonate, diisopropyl-1-peroxy-dicarbonate, di-n-propyl peroxidicarbonate, di-2-ethoxyethyl-peroxidicarbonate, and diallyl peroxidicarbonate.

Examples of diacyl peroxides include acetyl peroxide, benzoyl peroxide, decanoyl peroxide, 3,3,5-trimethylhexanoyl peroxide, 2,4-dichlorobenzoyl peroxide and lauroylperoxide.

Examples of dialkyl peroxiodes include di-t-butyl peroxide, dicumylperoxide, t-butylcumyl peroxide, 2,5-dimethyl-2,5-di(t-butylperpoxy)hexane, 1,3-bis(t-butylperoxyisopropyl)benzene and 2,5-dimethyl-2,5-di(t-butylperoxy)-3-hexane.

Examples of peroxyketals include 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-bis(t-butylperoxy)cyclohexane, 2,2-bis(t-butylperoxy)butane, 2,2-bis(t-butylperoxy)octane and 4,4-bis(t-butylperoxy)valeric acid-n-butylester.

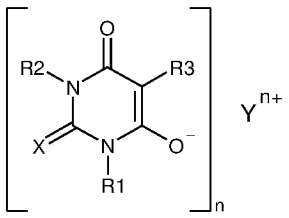
If a peroxy component is present, it is typically present in an amount of 0.1 to 5 wt.% or 0.25 to 4 wt.% of the dental composition.

In addition to peroxide components, further oxidizing components can be present, such as persulfate components, in particular water-soluble persulfate components.

Persulfates which can be used can be characterized by the formula $D_2S_2O_8$ with D being selected from Li, Na, K, NH_4, NR_4, with R being selected from H and CH_3. Examples of persulfate(s) which can be used include, $Na_2S_2O_8$, $K_2S_2O_8$, $(NH_4)_2S_2O_8$ and mixtures thereof.

If a persulfate component is present, it is typically present in an amount of 0.1 to 5 wt.% or 0.25 to 4 wt.%.

As reducing agent barbituric acid or thiobarbituric acid components, in particular the respective salts thereof, can be used. Suitable barbituric acid components may be characterized by the following formula:



with R1, R2, and R3 being independently selected from hydrogen, alkyl, substituted alkyl, alkenyl, cycloalkyl, substituted cycloalkyl, arylalkyl, aryl or substituted aryl; X being oxygen or sulfur; Y being a metal cation or organic cation.

The salt may comprise a metal cation or inorganic cation. Suitable metal cations include any metals M that are able to provide stable cations M^+, M^{2+}, or M^{3+}. Some possible inorganic cations include the cations of Li, Na, K, Mg, Ca, Sr, Ba, Al, Fe, Cu, Zn, or La.

Examples of suitable barbituric or thiobarbituric acid components include barbituric acid, thiobarbituric acid, 1,3,5-trimethylbarbituric acid, 1-phenyl-5-benzylbarbituric acid, 1-benzyl-5-phenylbarbituric acid, 1,3-dimethylbarbituric acid, 1,3-dimethyl-5-phenylbarbituric acid, 1-cyclohexyl-5-ethylbarbituric acid, 5-laurylbarbituric acid, 5-butylbarbituric acid, 5-allylbarbituric acid, 5-phenylthiobarbituric acid, 1,3-dimethylthiobarbituric acid,

trichlorobarbituric acid, 5-nitrobarbituric acid, 5-aminobarbituric acid, and 5-hydroxybarbituric acid.

An exemplary salt is the calcium salt of 1-benzyl-5-phenyl-barbituric acid. Another example of a suitable barbituric acid salt is the sodium salt of 1-benzyl-5-phenyl-barbituric acid. A possible salt is the calcium salt of 5-phenyl-thiobarbituric acid.

The salt may also comprise an organic cation. Suitable possible organic cations include the cations of amines, such as a cation of ammonium or a cation of alkylammonium. One example is the triethanolammonium salt of 1-benzyl-5-phenyl-barbituric acid.

If a barbituric acid or thiobarbituric acid component is present, it is typically present in an amount of 0.1 to 3 wt.% or 0.5 to 2 wt.% of the dental composition.

Other reducing agents which can be used include aromatic sulfinic acid salts or thiourea components.

Suitable sulfinic acid components may have the formula

$$R^1SOO\text{-}R^2,$$

in which R^1 is an alkyl, substituted alkyl, alkenyl, cycloalkyl, substituted cycloalkyl, arylalkyl, aryl or substituted aryl radical and R^2 = H, metal such as lithium, sodium or potassium or is an alkyl, substituted alkyl, alkenyl, cycloalkyl, substituted cycloalkyl, arylalkyl, aryl or substituted aryl radical.

If one of the radicals R^1 or R^2 is unsubstituted alkyl then this radical can be straight-chain or branched and can contain, for example, from 1 to 18 carbon atoms, preferably from 1 to 10, and in particular from 1 to 6 carbon atoms. Examples of low-molecular alkyl radicals are methyl, ethyl, propyl, isopropyl, n-butyl, t-butyl, isobutyl, n-pentyl, and isoamyl.

If one of the radicals R^1 or R^2 is a substituted alkyl radical then the alkyl moiety of this radical typically has the number of carbon atoms indicated above for unsubstituted alkyl. If one of the radicals R^1 or R^2 is alkoxyalkyl or alkoxycarbonylalkyl then the alkoxy radical contains, for example, from 1 to 5 carbon atoms and is preferably methyl, ethyl, propyl, isopropyl, n-butyl, t-butyl, isobutyl, n-pentyl or isoamyl. If one of the radicals R^1 or R^2 is haloalkyl then the halo moiety is understood to be fluoro, chloro, bromo or iodo.

If one of the radicals R^1 or R^2 is alkenyl, then it is typically a C_3 to C_5 alkenyl radicals, especially allyl. If one of the radicals R^1 or R^2 is unsubstituted cycloalkyl, then it is typically C_4 to C_7 cycloalkyl radicals, such as cyclopentyl or cyclohexyl. If one of the radicals R^1 or R^2 is substituted cycloalkyl, then it is typically one of the above-indicated cycloalkyl radicals,

with the substituent or substituents on the cycloalkyl radical possibly being, for example, C_1 to C_4 alkyl such as methyl, ethyl, propyl, n-butyl or isobutyl, fluoro, chloro, bromo, iodo or C_1 to C_4 alkoxy, especially methoxy. If one of the radicals R^1 or R^2 is aryl or aralkyl, then it is typically a phenyl or naphthyl as aryl. Preferred arylalkyl radicals include benzyl and phenylethyl.

R^1 or R^2 may also be substituted aryl radicals if desired. In this case phenyl and naphthyl are preferred and as ring substituents C_1 to C_4 alkyl, especially methyl, halogen or C_1 to C_4 alkoxy, especially methoxy.

In particular the following components were found to be useful: benzenesulfinic acid, sodium benzenesulfinate, sodium benzenesulfinate dihydrate, sodium toluenesulfinate, formamidinesulfinic acid, sodium salt of hydroxymethanesulfinic acid, sodium salt of 2,5-dichlorobenzenesulfinic acid, 3-acetamido-4-methoxybenzenesulfinic acid, wherein sodium toluenesulfinate or sodium benzenesulfinate and their hydrates are sometime preferred.

If a sulfinic acid component is present, it is typically present in an amount of 0.1 to 3 wt.% or 0.5 to 2 wt.% of the dental cement composition.

Suitable thiourea components include 1-ethyl-2-thiourea, tetraethyl thiourea, tetramethyl thiourea, 1,1-dibutyl thiourea, and 1,3-dibutyl thiourea and mixtures thereof.

If desired, the dental cement composition may contain a combination or mixture of different reducing agents, including a combination of barbituric acid components and sulfinic acid components.

Besides the above-described components, the redox-initiator system may also comprise activators.

Suitable activators include, tertiary aromatic amines, such as the N,N-bis-(hydroxyalkyl)-3,5-xylidines (e.g. described in US 3,541,068) as well as N,N-bis-(hydroxyalkyl)-3,5-di-t-butylanilines, in particular N,N-bis-([beta]-oxybutyl)-3,5-di-t-butylaniline as well as N,N-bis-(hydroxyalkyl)-3,4,5-trimethylaniline.

If desired and for acceleration, the polymerization can also be carried out in the presence of a transition metal component. Suitable transition metal component(s) include organic and/or inorganic salt(s) of vanadium, chromium, manganese, iron, cobalt, nickel, and/or copper, with copper, iron and vanadium being sometimes preferred.

According to one embodiment, the transition metal component is a copper containing component. The oxidation stage of copper in the copper containing component(s) is preferably +1 or +2.

Typical examples of copper component(s) which can be used include salts and complexes of copper including copper acetate, copper chloride, copper benzoate, copper acetylacetonate, copper naphthenate, copper carboxylates, copper bis(1-phenylpentan-1,3-dione) complex (copper procetonate), copper ethylhexanoate, copper salicylate, complexes of copper with thiourea, ethylenediaminetetraacetic acid and/or mixtures thereof. The copper compounds can be used in hydrated form or free of water.

Especially preferred are sometimes copper(II) acetate, copper bis(1-phenylpentan-1,3-dione) complex (copper procetonate), and copper ethylhexanoate.

According to one embodiment, the transition metal component is an iron containing component. The oxidation stage of iron in the iron containing component(s) is preferably +2 or +3.

Typical examples of iron containing component(s) which can be used include salts and complexes of iron including Fe(III) sulfate, Fe(III) chloride, iron carboxylates, iron naphthenate, Fe(III) acetylacetonate including the hydrates of these salts.

According to one embodiment, the transition metal component is a vanadium containing component. The oxidation stage of vanadium in the vanadium containing component(s) is preferably +4 or +5.

Typical examples of vanadium component(s) which can be used include salts and complexes of vanadium including vanadium acetylacetonate, vanadyl acetylacetonate, vanadyl stearate, vanadium naphthenate, vanadium benzoyl acetonate, vanadyl oxalate, bis(maltolato)oxovanadium (IV), oxobis(1-phenyl-1,3-butanedionate)vanadium (IV), vanadium (V) oxytriisopropoxide, ammonium metavanadate (V), sodium metavanadate (V), vanadium pentoxide (V), divanadium tetraoxide (IV), and vanadyl sulfate (IV) and mixtures thereof, with vanadium acetylacetonate, vanadyl acetylacetonate, and bis(maltolato)oxovanadium (IV) being sometimes preferred.

Suitable redox initiator systems are also described in US 2003/008967 A1 (Hecht et al.), US 2004/097613 A1 (Hecht et al.), US 2019/000721 A1 (Ludsteck et al.). The content of these references is herewith incorporated by reference.

The compositions may also contain suitable adjuvants or additives such as surfactants, rheology modifiers, retarders, stabilizers, pigments, dyes, photo bleachable colorants, fluoride release agents, solvents and other ingredients known to those skilled in the art.

Surfactants which can be added include polyethylene glycol modified siloxanes (e.g. Silwet™ type surfactants available from Momentive) and polyethylene glycol modified carbosilanes (described e.g. in US 5,750,589 (Zech et al.).

Rheology modifiers which can be added include surface modified fumed silica as described above, organophilic phyllosilicates, modified ureas, polyhydroxycarboxylic acid amides (e.g. Rheobyk™ types available from Byk-Chemie, Wesel, Germany), dibenzylidene sorbitol, and diamides (e.g. Thixatrol™ types available from Elementis, East Windsor, New Jersey, USA).

Retarders which can be added include 1,2-diphenyl ethylene, and derivatives thereof.

Stabilizers which can be used include especially free radical scavengers such as substituted and/or unsubstituted hydroxyaromatics (e.g. butylated hydroxytoluene (BHT), hydroquinone, hydroquinone monomethyl ether (MEHQ), 3,5-di-tert-butyl-4-hydroxy-anisole (2,6-di-tert-butyl-4-ethoxyphenol), 2,6-di-tert-butyl-4-(dimethylamino)methylphenol or 2,5-di-tert-butyl hydroquinone, 2-(2'-hydroxy-5'-methylphenyl)-2H-benzotriazole, 2-(2'-hydroxy-5'-t-octylphenyl)-2H-benzotriazole, 2-hydroxy-4-methoxybenzophenone (UV-9), 2-(2'-hydroxy-4',6'-di-tert-pentylphenyl)-2H-benzotriazole, 2-hydroxy-4-n-octoxybenzophenone, 2-(2'-hydroxy-5'-methacryloxyethylphenyl)-2H-benzotriazole, phenothiazine, and HALS (hindered amine light stabilizers).

Pigments and/or dyes which can be used include titanium dioxide or zinc sulphide (lithopones), red iron oxide 3395, Bayferrox™ 920 Z Yellow, Neazopon™ Blue 807 (copper phthalocyanine-based dye) or Helio™ Fast Yellow ER. These additives may be used for individual coloring of the compositions.

Examples of photo bleachable colorants include Rose Bengal, Methylene Violet, Methylene Blue, Fluorescein, Eosin Yellow, Eosin Y, Ethyl Eosin, Eosin bluish, Eosin B, Erythrosin B, Erythrosin Yellowish Blend, Toluidine Blue, 4',5'-Dibromofluorescein and blends thereof. Further examples of photo bleachable colorants can be found in US 6,444,725 (Trom et al.).

Examples of fluoride release agents include naturally occurring or synthetic fluoride minerals. These fluoride sources can optionally be treated with surface treatment agents.

Solvents, which can be present include linear, branched or cyclic, saturated or unsaturated alcohols, ketones, esters, ethers or mixtures of two or more of said type of solvents with 2 to 10 C atoms. Preferred alcoholic solvents include methanol, ethanol, iso-propanol and n-propanol. Other suitable organic solvents are THF, acetone, methyl ethyl ketone, cyclohexanol, toluene, alkanes and acetic acid alkyl esters, in particular acetic acid ethyl ester.

There is no need for these additive(s) to be present, so additive(s) might not be present at all. However, if present they are typically present in an amount which is not detrimental to the intended purpose.

Additives are typically present in the following amounts: at least 0 or 0.01 or 0.1 wt.%; utmost 20 or 15 or 10 wt.%; in the range of 0 to 20; or 0.01 to 15; or 0.1 to 10 wt.%; wt.% with respect to the dental composition.

The dental composition comprises, essentially consists of or consists of the following components:

a. surface-treated filler, particularly in an amount of 40 to 80 wt.%,
b. curable components, particularly in an amount of 5 to 50 wt.%,
c. initiator system suitable for curing the curable components, particularly in an amount of 0.1 to 5 wt.%,
d. additives, particularly in an amount of 0 to 10 wt.%,

wt.% with respect to the weight of the dental composition.

The dental composition described in the present text is typically produced by combining or mixing the respective components, i.e. the polymerizable components of the resin matrix, the fillers and the initiator components together with other optional components, such as additives. Usually, the resin matrix is provided first and the filler is added later.

If desired, a speed mixer can be used. Depending on the components to be mixed, the mixing is done under save light conditions. Mixing also includes kneading. If desired during or at the end of the mixing vacuum can be applied for removing air which has been introduced during the mixing or kneading.

The dental composition described in the present text is typically for use in a method of restoring a tooth in the mouth of a mammal, wherein the dental composition is as described in the present text, and wherein the method comprises the steps of

a) bringing the dental composition in contact with the surface of the tooth to be restored,
b) curing the dental composition by applying radiation.

More particularly, the process may comprise the steps of

a) applying the dental composition to the surface of hard dental tissue; if desired, the surface of the hard dental tissue can be an etched surface (e.g., with phosphoric acid) or a non-etched surface,

b) optionally dispersing the dental composition to a thin film, preferably using a stream of air,

c) radiation curing of the dental composition.

For the curing step, typically a dental curing light is used. The radiation usually has a wavelength in the range of 400 to 800 nm and is applied for a time period in the range of 5 s to 1 min.

The dental composition is in particular useful in the dental and orthodontic field. The dental composition can be used as or for producing a dental restoration.

Examples of dental restorations include direct restorative materials (e.g., anterior and posterior restoratives), prostheses, veneers, artificial crowns, artificial teeth, dentures, and the like.

The term "prosthesis" as used herein refers to a composite that is shaped and polymerized for its final use (e.g., as a crown, bridge, veneer, inlay, onlay or the like) before it is disposed adjacent to a tooth.

When the dental material is applied to a tooth, the tooth can optionally be pre-treated with a primer such as dentin or enamel adhesive by methods known to those skilled in the art.

In particular, the dental composition may be used as composite filling material, cavity liner, or fixing material for orthodontic appliances.

The term "composite filling material" refers to a filled dental composition. A dental composite material is typically used for restoring a defect tooth structure in the mouth of a patient.

A “cavity liner” means a composition for protecting the pulp before a composite filling material or dental restoration is applied.

In a preferred aspect, the dental material is a low-viscous dental filling material.

A further aspect of the invention is directed to the use of the surface-treated filler described in the present text for reducing the viscosity of a dental composition comprising curable components and filler in an amount of 40 to 80 t.% with respect to the weight of the dental composition.

The surface-treated filler is in particular useful for producing a hardenable dental composition having a filler content of 40 to 80 wt.% and a viscosity of 5 to 1,500 Pa*s at 25°C and a shear rate of 0.01 s^{-1} if no rheological modifiers are present.

In a further aspect, the invention is related to the following embodiments:

Embodiment 1

A dental composition comprising, essentially consisting of or consisting of
surface-treated filler in an amount of 40 to 80 wt.%,
curable components selected from polymerizable components comprising an acidic moiety, polymerizable components not comprising an acidic moiety, and mixtures thereof, in an amount of 5 to 50 wt.%,
initiator system suitable for curing the curable components comprising a photo-initiator system and/or redox-initiator system, in an amount of 0.1 to 5 wt.%,
additives in an amount of 0 to 10 wt.%,
wt.% with respect to the weight of the dental composition,
the surface-treating agent being characterized by the following features:
comprising only one (meth)acrylate moiety,
comprising at least one tri-methoxysilane or tri-ethoxysilane moiety,
comprising only one urethane moiety,
comprising one linear alkylene moiety AM1 connecting the (meth)acrylate moiety to the urethane moiety, the linear alkylene moiety AM1 comprising 6 to 12 C-atoms,
comprising one linear alkylene moiety AM2 connecting the at least one tri-methoxysilane or tri-ethoxysilane moiety with the urethane moiety, the linear alkylene moiety AM2 comprising 1 to 4 C-atoms.

Embodiment 2

A dental composition comprising, essentially consisting of or consisting of
surface-treated filler, the filler particles being selected from non-aggregated, non-agglomerated nano-sized particles of SiO_2, ZrO_2 or mixtures thereof, aggregated nano-sized particles of SiO_2, ZrO_2, or mixtures thereof, agglomerated nano-sized particles of SiO_2, ZrO_2, Al_2O_3, or mixtures thereof, non acid-reactive particles of glasses, silicas, metal oxides or mixtures thereof, acid-reactive particles of glasses, metal oxides and hydroxide or mixtures thereof, in an amount of 40 to 80 wt.%,
curable components selected from polymerizable components comprising an acidic moiety, polymerizable components not comprising an acidic moiety, and mixtures thereof, in an amount of 5 to 50 wt.%,

initiator system suitable for curing the curable components comprising a photo-initiator system and/or redox-initiator system in an amount of 0.1 to 5 wt.%,
additives in an amount of 0 to 10 wt.%,
wt.% with respect to the weight of the dental composition,
the surface-treating agent being characterized by the following features:
comprising only one (meth)acrylate moiety,
comprising at least one tri-methoxysilane or tri-ethoxysilane moiety,
comprising only one urethane moiety,
comprising one linear alkylene moiety AM1 connecting the (meth)acrylate moiety to the urethane moiety, the linear alkylene moiety AM1 comprising 6 to 12 C-atoms,
comprising one linear alkylene moiety AM2 connecting the at least one tri-methoxysilane or tri-ethoxysilane moiety with the urethane moiety, the linear alkylene moiety AM2 comprising 1 to 4 C-atoms.

Embodiment 3

A dental composition comprising, essentially consisting of or consisting of
surface-treated filler in an amount of 40 to 80 wt.%,
curable components selected from polymerizable components comprising an acidic moiety, polymerizable components not comprising an acidic moiety, and mixtures thereof, in an amount of 5 to 50 wt.%,
initiator system suitable for curing the curable components comprising a photo-initiator system and/or redox-initiator system in an amount of 0.1 to 5 wt.%,
additives in an amount of 0 to 10 wt.%,
wt.% with respect to the weight of the dental composition,
the surface-treating agent being characterized by the following formula:

$$H_2C=CHR^1\text{-}CO\text{-}O\text{-}(CH_2)_n\text{-}X\text{-}CO\text{-}Y\text{-}(CH_2)_m\text{-}Si(R^2)_o(R^3)_{3-o}$$

with R^1 = H or CH_3; R^2 = independently selected from Cl, Br, O-C_{1-4} alkyl, O-C_{1-4} acyl; R^3 = independently selected from C_{1-4} alkyl; X = O; Y = NH; n = 6-12; m = 1-4; o = 1-3.

Embodiment 4

A dental composition comprising, essentially consisting of or consisting of
surface-treated filler, the filler particles being selected from aggregated nano-sized particles of SiO_2, ZrO_2, or mixtures thereof, agglomerated nano-sized particles of SiO_2, ZrO_2, Al_2O_3, or mixtures thereof, in an amount of 40 to 80 wt.%,

curable components selected from polymerizable components comprising an acidic moiety, polymerizable components not comprising an acidic moiety, and mixtures thereof, in an amount of 5 to 50 wt.%,

initiator system suitable for curing the curable components comprising a photo-initiator system and/or redox-initiator system in an amount of 0.1 to 5 wt.%,

additives in an amount of 0 to 10 wt.%,

wt.% with respect to the weight of the dental composition,

the surface-treating agent being characterized by the following features:

comprising only one (meth)acrylate moiety,

comprising at least one tri-methoxysilane or tri-ethoxysilane moiety,

comprising only one urethane moiety,

comprising one linear alkylene moiety AM1 connecting the (meth)acrylate moiety to the urethane moiety, the linear alkylene moiety AM1 comprising 6 to 12 C-atoms,

comprising one linear alkylene moiety AM2 connecting the at least one tri-methoxysilane or tri-ethoxysilane moiety with the urethane moiety, the linear alkylene moiety AM2 comprising 1 to 4 C-atoms.

The dental composition described in the present text does typically not contain bisphenol-A-glycidyl methacrylate (Bis-GMA), in particular in an amount of 1 wt.% or more, wt.% with respect to the weight of the dental composition. Thus, this component is typically not present and/or has not been wilfully added.

The dental composition is typically provided to the practitioner under hygienic conditions. During storage, the composition is typically packaged in a suitable packaging and/or delivery device.

One possibility to achieve this includes packing or storing the composition in a sealed container. A suitable container may have a front end and a rear end, a piston movable in the container and a nozzle or cannula for delivering or dispensing the composition located in the container. The container has usually only one compartment or reservoir. The volume of the container is typically in the range of 0.1 to 100 ml or 0.5 to 50 ml or 1 to 30 ml.

A suitable single-use container may have a volume in the range of 0.05 to 1 ml. This is the volume typically needed for a single application procedure. Such a container is typically used only once (e.g., disposable packing).

The composition can be dispensed out of the container by moving the piston in the direction of the nozzle. The piston can be moved either manually or with the aid of an application

device or applier designed to receive the container (e.g., an application device having the design of a caulk gun).

Examples of containers which can be used include compules, syringes and screw tubes.

The compule has typically a cylindrical housing with a front and a rear end and a nozzle. The rear end of the housing is usually sealed with a movable piston. Typically, the dental composition is dispensed out of the compule or container using an applier having a movable plunger (e.g., an application device having the shape of a caulk gun).

Examples of suitable compules or containers are described in US 5,624,260 (Wilcox et al.), EP 1 340 472 A1 (Centrix), US 2007/0172789 A1 (Mueller et al.), and US 5,865,803 (Major). Further suitable containers are exemplified in US 5,927,562 (Hammen et al) and US 2011/151403 A1 (Pauser et al.).

It can be advantageous, if a container is used comprising a nozzle having a shape and size, which allows an easy and safe application of the composition to the soft dental tissue surrounding the tooth to be restored, also near the interdental region.

The smaller the diameter of the nozzle is, the easier the nozzle can be placed into the region between two teeth. However, a small diameter of the nozzle may result in an increase of the extrusion force needed for dispensing the composition out of the device. Thus, not all cannula sizes and diameters are equally suitable. A device with a nozzle or cannula having an external diameter in the range from 0.6 mm to 1.3 mm and an internal diameter in the range from 0.2 mm to 0.9 mm has been found to be particular useful.

Flowable dental composite materials are often stored in a packaging material having the shape of a syringe.

A packaging device may also comprise two compartments, wherein each compartment is equipped with a nozzle for delivering the composition or parts stored therein. Once delivered in adequate portions, the parts can then be mixed by hand on a mixing plate.

Packaging devices with two compartments are in particular suitable for storing and delivering two part composition, i.e. compositions which need to be kept separate before use in order to avoid an undesired polymerization. Two part compositions are typically cured by a redox-initiator system, where the part containing the oxidizing agent is kept separate from the part containing the reducing agent.

The packaging device may have an interface for receiving a static mixing tip. The mixing tip is used for mixing the respective compositions.

The packaging device typically comprises two housings or compartments having a front end with a nozzle and a rear end and at least one piston movable in the housing or compartment.

Cartridges which can be used are also described e.g., in US 2007/0090079 A1 or US 5,918,772. Some of the cartridges which can be used are commercially available e.g., from SulzerMixpac company (Switzerland).

Static mixing tips which can be used are described e.g., in US 2006/0187752 A1 or in US 5,944,419, the disclosure of which is incorporated by reference. Mixing tips which can be used are commercially available from Sulzer Mixpac (Switzerland), as well.

Other suitable storing devices are described e.g., in WO 2010/123800 A1 (3M), WO 2005/016783 A1 (3M), WO 2007/104037 A1 (3M), WO 2009/061884 A1 (3M), in particular the device shown in Fig. 14 of WO 2009/061884 A1 (3M) or WO 2015/073246 A1 (3M), in particular the device shown in Fig. 1 of WO 2015/07346 A1. Those storing devices have the shape of a syringe.

The invention also relates to a kit of parts comprising the dental composition descried in the present text and the following parts alone or in combination: dental adhesive; dental curing light; application device.

Dental adhesives are typically acidic dental composition with a rather low viscosity (e.g., 0.01 to 3 Pa*s at 25°C). Dental adhesives directly interact with the enamel or dentin surface of a tooth. Dental adhesives are typically one-part compositions, are radiation-curable and comprise ethylenically unsaturated component(s) with acidic moiety, ethylenically unsaturated component(s) without acidic moiety, water, sensitizing agent(s), reducing agent(s) and additive(s).

Examples of dental adhesives are described in US 2020/0069532 A1 (Thalacker et al.) and US 2017/0065495 A1 (Eckert et al.). Dental adhesives are also commercially available, e.g., 3M™ Scotchbond™ Universal (3M Oral Care).

Suitable dental curing lights are described in US 10,758,126 B2 (Geldmacher et al.) or US 10,231,810 B2 (Gramann et al). Dental curing lights are also commercially available, e.g., 3M™ Elipar™ S10 or 3M™ Elipar™ DeepCure S LED curing light (3M Oral Care).

Suitable application devices include e.g., brushes, spatula, syringes and other suitable equipment known to the skilled person.

The complete disclosures of the patents, patent documents, and publications cited herein are incorporated by reference in their entirety as if each were individually incorporated. Various modifications and alterations to this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention. The above specification, examples and data provide a description of the manufacture and use of the compositions and methods of the invention. The invention is not limited to the embodiments disclosed herein. One skilled in the art will appreciate that many alternative embodiments of the invention can be made without departing from the spirit and scope of thereof.

The following examples are given to illustrate the invention.

Examples

Unless otherwise indicated, all parts and percentages are on a weight basis, all water is de-ionized water, and all molecular weights are weight average molecular weight. Moreover, unless otherwise indicated all experiments were conducted at ambient conditions (23°C; 1013 mbar).

Methods

Viscosity

Viscosity measurements were taken on a rheometer equipped with a plate-plate system (d=15mm or 20mm) using a 0.2mm gap at 25°C, and ramping shear from 100/s – 0.008/s in 1min.

Particle Size (suitable for micro-sized particles)

If desired, the particle size distribution including the particle size (d50) per volume can be determined by laser diffraction with a Mastersizer 2000 (Malvern) particle size detection device applying the Fraunhofer approximation. During the measurement, ultrasonic is typically used to accurately disperse the sample. For water-insoluble particles, water is typically used as dispersant.

Particle Size (suitable for nano-sized particles)

If desired, particle size measurements can made using a light scattering particle sizer equipped with a red laser having a 633 nm wavelength of light (obtained under the trade designation “ZETA SIZER - Nano Series, Model ZEN3600” from Malvern Instruments Inc., Westborough, MA). Each sample is analyzed in a one-centimeter square polystyrene sample cuvette. The sample is diluted 1:100, e.g. 1 g of sample is given to 100 g of de-ionized water and mixed. The sample cuvette is filled with about 1 gram of diluted sample. The sample cuvette is then placed in the instrument and equilibrated at 25°C. The

instrument parameters are set as follows: dispersant refractive index 1.330, dispersant viscosity 0.8872 mPa*s, material refractive index 1.43, and material absorption value 0.00 units. The automatic size-measurement procedure is then run. The instrument automatically adjusts the laser-beam position and attenuator setting to obtain the best measurement of particle size.

The light scattering particle-sizer illuminates the sample with a laser and analyzes the intensity fluctuations of the light scattered from the particles at an angle of 173 degrees. The method of Photon Correlation Spectroscopy (PCS) can be used by the instrument to calculate the particle size. PCS uses the fluctuating light intensity to measure Brownian motion of the particles in the liquid. The particle size is then calculated to be the diameter of sphere that moves at the measured speed.

The intensity of the light scattered by the particle is proportional to the sixth power of the particle diameter. The Z-average size or cumulant mean is a mean calculated from the intensity distribution and the calculation is based on assumptions that the particles are mono-modal, mono-disperse, and spherical. Related functions calculated from the fluctuating light intensity are the Intensity Distribution and its mean. The mean of the Intensity Distribution is calculated based on the assumption that the particles are spherical. Both the Z-average size and the Intensity Distribution mean are more sensitive to larger particles than smaller ones.

The Volume Distribution gives the percentage of the total volume of particles corresponding to particles in a given size range. The volume-average size is the size of a particle that corresponds to the mean of the Volume Distribution. Since the volume of a particle is proportional to the third power of the diameter, this distribution is less sensitive to larger particles than the Z-average size. Thus, the volume-average will typically be a smaller value than the Z-average size. In the scope of this document the Z-average size is referred to as “mean particle size”.

pH value

If desired, the pH value of can be determined as follows: 1.0 g of the material to be tested is dispersed in 10 ml deionized water and stirred for about 5 min. A calibrated pH electrode is dipped into the suspension and the pH value is determined during stirring.

Elemental Composition

If desired, the elemental composition can be determined by X-ray fluorescence spectrometry (XRF), e.g. with the ZSX Primus II from Rigaku, Japan.

Flexural strength (FS)

If desired, flexural strength can be determined by conducting a three-point flexural strength test according to ISO 4049:2019 using test specimen having the size 2*2*25 mm. The flexural strength is given in MPa.

Flexural Modulus (FM)

If desired, the flexural modulus can be determined together with the flexural strength test using a universal testing machine (e.g. Zwick) as slope of the linear-elastic part of the stress-strain-curve. The flexural modulus is given in GPa.

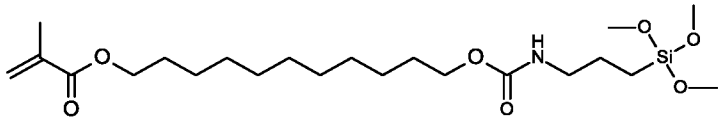
Materials

Material Designation	Description	possible source of supply
EtOAc	Ethyl Acetate	EMD Millipore, Burlington, MA
DMF	Dimethylformamide	EMD Millipore, Burlington, MA
KI	Potassium iodide	EMD Millipore, Burlington, MA
KOH	Potassium hydroxide	EMD Millipore
HEMA	2-Hydroxyethyl methacrylate	
NaI	Sodium iodide	Alfa Aesar
K-Kat XK-672	zinc/zirconium catalyst	King Industries, Waterbury CT
DS	Decyltrimethoxysilane	
GM32087 (UF 0.4)	Dental glass based on SrO_2; Al_2O_3, B_2O_3, SiO_2; average partile size: 0.4 µm	Schott AG, Landshut, Germany
SiO2/ZrO2	silica-zirconia nanocluster filler, prepared generally as described in US 6,730,156 at column 25, lines 50-63 (Preparatory Example A)	
BisEMA2	Ethoxylated bisphenol A dimethacrylate (~ 2 EO units per mole)	Sartomer, Arkema Group
UDMA	Urethanedimethacrylate	Evonik Performance Materials GmbH, Darmstadt Germany
TEGDMA	Triethylenglycoldimethacrylate	TCI Europe
CPQ	Camphorquinone	Sigma Aldrich, Steinheim Germany
EDMAB	Ethyl-diamino-ethyl-benzoate	Alfa Aeser GmbH & Co KG Karlsruhe Germany
DPIPF6	Diphenyl-iodonium-hexafluoro phosphate	Alfa Aeser GmbH & Co KG Karlsruhe, Germany
BHT	Butylated hydroxytoluene	OQEMA GmbH, Mönchengladbach, Germany

T R796	2-(2'-Hydroxy-5' meth-acryloxyethylphenyl)-2H-benzotriazole	Ciba Speciality Chemicals Corp., NY
GF31	3-Methacryloxypropyl-trimethoxysilane	
PGME	1-Methoxy-2-propanol	

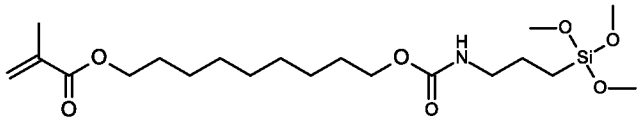
Table 1

Synthesis of 11-(3-trimethoxysilylpropylcarbamoyloxy)undecyl 2-methylprop-2-enoate (C11 Methoxy)



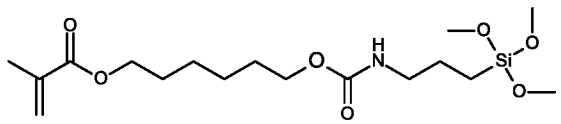
11-Hydroxyundecyl 2-methylprop-2-enoate (35.0g, 137 mmol) was charged into a 3 neck RBF 250 mL fitted with internal thermometer and magnetic stirrer, and 3-Isocyanatopropyl-trimethoxysilane (29.0 g, 141 mmol) was added and the mixture was stirred for 48 h at 60° C. Infrared absorption analysis indicated complete consumption of the isocyanate.

Synthesis of 9-(3-trimethoxysilylpropylcarbamoyloxy)nonyl 2-methylprop-2-enoate (C9 Methoxy)



9-Hydroxynonyl 2-methylprop-2-enoate (35.0g, 153 mmol) was charged into a 3 neck 250 mL RBF fitted with internal thermometer and magnetic stirrer, and 3-Isocyanatopropyl-trimethoxysilane (32.5 g, 158 mmol) was added and the mixture was stirred for 48 h at 60° C. Infrared absorption analysis indicated complete consumption of the isocyanate.

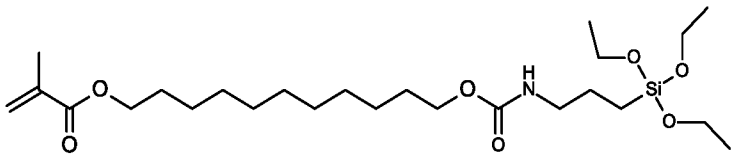
Synthesis of 6-(3-trimethoxysilylpropylcarbamoyloxy)hexyl 2-methylprop-2-enoate (C6 Methoxy)



6-Hydroxyhexyl 2-methylprop-2-enoate (35.0g, 188 mmol) was charged into a 3 neck 250 mL RBF fitted with internal thermometer and magnetic stirrer, and 3-Isocyanatopropyl-trimethoxysilane (40.0 g, 195 mmol) was added and the mixture was

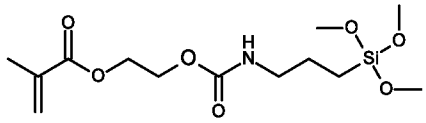
stirred for 48 h at 60° C. Infrared absorption analysis indicated complete consumption of the isocyanate.

Synthesis of 11-(3-triethoxysilylpropylcarbamoyloxy)undecyl 2-methylprop-2-enoate (C11 ethoxy)



11-Hydroxyundecyl 2-methylprop-2-enoate (24.0 g, 93.6 mmol) was charged into a flask, and 3-Isocyanatopropyltriethoxysilane (23.1g, 93.4 mmol) was added and the mixture was stirred for 48 h at 60° C. Infrared absorption analysis indicated complete consumption of the isocyanate.

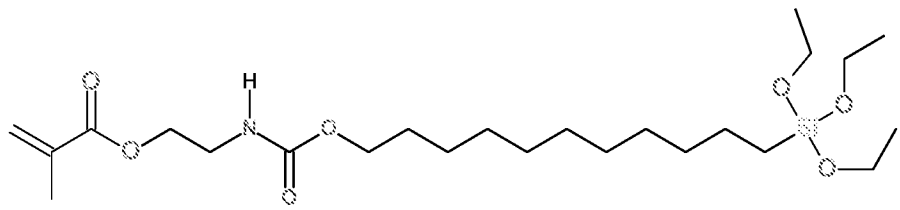
Synthesis 2-(3-trimethoxysilylpropylcarbamoyloxy)ethyl 2-methylprop-2-enoate (C2 methoxy)



3-Isocyanatopropyltrimethoxysilane (34.46g, 0.1678 mol) and K-Kat XK-672 (0.055g, 1000 ppm based on total solids) were charged into a flask and cooled. Next HEMA (20.54g, 0.1578 mol) was added dropwise. The reaction was monitored by FTIR for the presence of the -NCO peak at 2265 cm^{-1}.

M-C2-U-C11-TMS

M-C2-U-C11-TMS, was prepared according to US 10,975,229 B1 (column 50; Comparative Synthesis Example 1).



Surface-Treatment of Fillers

Glass Filler (G)

Filler GM32087 (UF 0.4), ethanol (ratio 1:2), and 1 wt.% (with respect to the filler weight) of 25% aqueous ammonia was added to the slurry. were mixed for 3 hrs in an ultrasonic bath and then silane was added.

The mixture was stirred 3h at RT and then the solvent was removed at 45 °C in a rotary evaporator (~20mbar), screened with a 200 micron sieve, and then further evaporated for 1 h at 100°C in a rotary evaporator (~20mbar).

Silica-Zirconia Cluster Filler (SiO2/ZrO2)

The respective silane (10.5% with respect to the weight of the filler) was dissolved in either ethyl acetate (EtOAc) or 1-methoxy-2-propanol (PGME). Solvents were used at a rate of 100% to 200% with respect to the weight of the filler. A magnetic stir bar was used to mix the silane into the solvent.

Filler SiO2/ZrO2 cluster was added slowly to the solution, ensuring that the magnetic stir bar continued to stir the solution as its viscosity increased due to filler addition. Once the filler was added, 2 wt.% (with respect to the filler weight) of 30% aqueous ammonia was added to the slurry. If EtOAc was used, the slurry was allowed to react at room temperature overnight. The slurry was dried by pouring it into a glass casserole dish and evaporating the ethyl acetate in a solvent oven set to 85°C for 90 min. The filler was then screened through a 70 micron sieve. If PGME was used, after addition of the ammonia the slurry was placed onto a rotovap and heated to 85°C for 1 h. It is then dried in the glass tray like the other.

Resin for Glass Filler (Re-G)

The following resin was used: BisEMA2 (68.8 wt.%), UDMA (19.7 wt.%), TEGDMA (9.8 wt.%), CPQ (0.16 wt.%), DPIFP6 (0.3 wt.%), EDMAB (0.6 wt.%), BHT (0.09 wt.%), T R796 (0.6 wt.%).

The resin composition was prepared by mixing and slightly heating the components under save light conditions until a clear solution was formed.

Resin for Silica-Zirconia Cluster Filler (Re-SiO_2/ZrO_2)

The following resin was used: BisEMA2 (78.6%), TEGDMA (19.65%), CPQ (0.16%), DPIFP6 (0.3%), EDMAB (0.6%), BHT (0.09%), T R796 (0.6%).

The resin composition was prepared by mixing and slightly heating the components under save light conditions until a clear solution was formed.

Curable Composition

The surface-treated filler was mixed/kneaded with the resin composition until a homogenous composition was obtained. For mixing a Flak-Tek speedmixer was used. The composition was degassed by applying vacuum as appropriate.

The content of glass filler G in composition Re-G was 65 wt.%. The content of cluster filler SiO2/ZrO2 in composition Re-SiO2/ZrO2 was 66 wt.%.

The obtained compositions were filled into syringes and centrifugated. The compositions were further analyzed with respect to viscosity (at various shear rates), flexural strength and flexural modulus (Tables 2 and 3).

			Viscosity (Pa•s)		
Example (SiO2/ZrO2 Filler)	Coupling Agent	Solvent	@ 0.01/s	@ 1/s	@ 100/s
Ex 1	C11-Ethoxy	PGME	14	10	12
Ex 2	C11-Methoxy	EtOAc	204	19	10
Ex 3	C9-Methoxy	EtOAc	21	8	10
Ex 4	C6-Methoxy	EtOAc	7	7	11
C.E. 1	C2-Methoxy	EtOAc	3,410	388	22
C.E. 2	GF31	PGME	6,011	266	24
C.E. 3	M-C2-U-C11-TMS	EtOAc	7,086	516	16

Table 2 – Re-SiO2/ZrO2; C.E.: Comparative Example

Example (Glass)		Viscosity (Pa*s)				
	Coupling Agent	@ 0.01/s	@ 1/s	@ 100/s	FS (MPa)	FM (GPa)
Ex 5	C11-Ethoxy	1,455	58	24	146	6.2
Ex 6	C11-Methoxy	942	40	13	149	6.0
Ex 7	C9-Methoxy	107	17	18	138	5.5
Ex 8	C6-Methoxy	388	30	21	125	5.4
C.E. 4	C2-Methoxy	2,962	240	105	146	6.9
C.E. 5	GF31	9,765	359	65	143	6.6

Table 3 – Re-G; C.E.: Comparative Example

Table 2 and 3 show the viscosity profiles of different compositions using various silane surface-treated fillers.

As can be seen, the use of surface-treated fillers according to the invention results in desirable low viscosity of a curable composition containing such a filler at a low shear rate. A nearly Newtonian fluid behavior was observed.

On the other hand, as shown in the comparative examples the use of surface-treated fillers with short alkylene bridging moieties results in an undesirable high viscosity at a low shear rate.

Claims

1. A dental composition comprising curable components and a surface-treated filler, the surface-treated filler comprising filler particles the surface of which has been treated with a surface-treating agent, the surface-treating agent being characterized by the following features:
   comprising at least one (meth)acrylate moiety,
   comprising at least one hydrolysable silane moiety,
   comprising only one urethane moiety,
   comprising a linear alkylene moiety AM1 connecting the at least one (meth)acrylate moiety to the urethane moiety,
   comprising a linear alkylene moiety AM2 connecting the at least one hydrolysable silane moiety with the urethane moiety, and
   the linear alkylene moiety AM1 comprising more carbon atoms than the linear alkylene moiety AM2.

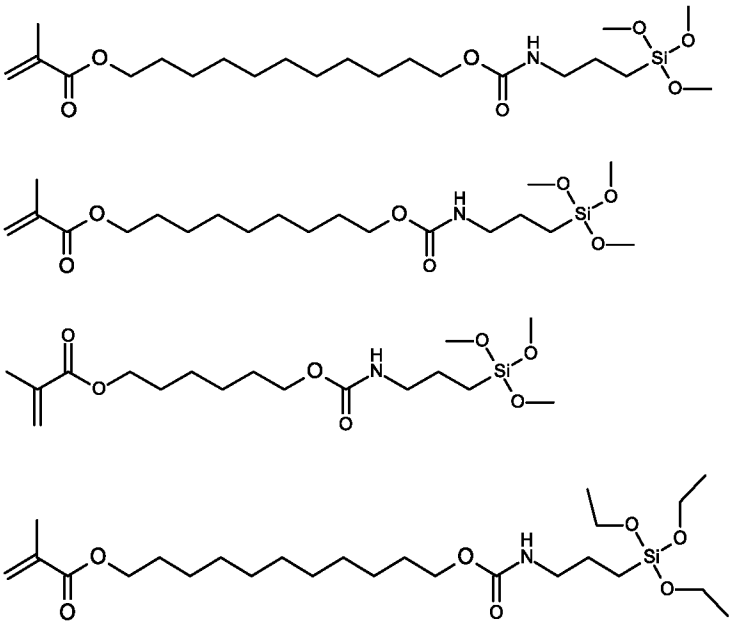
2. The dental composition according to the preceding claim, the surface-treating agent being characterized by the following features:
   comprising only one (meth)acrylate moiety,
   comprising at least one hydrolysable silane moiety, preferably selected from
   $$-Si(R^2)_o(R^3)_{3-o}$$
   with R^2 = independently selected from Cl, Br, O-C_{1-4} alkyl, O-C_{1-4} acyl; R^3 = independently selected from C_{1-4} alkyl; o = 1-3,
   comprising only one urethane moiety,
   comprising one linear alkylene moiety AM1 connecting the (meth)acrylate moiety to the one urethane moiety, the linear alkylene moiety AM1 comprising 6 to 12 C-atoms, and
   comprising one linear alkylene moiety AM2 connecting the at least one hydrolysable silane moiety with the urethane moiety, the linear alkylene moiety AM2 comprising 1 to 4 C-atoms.

3. The dental composition according to any of the preceding claims, the surface-treating agent being characterized by the following formula:
   $$H_2C=CHR^1\text{-}CO\text{-}O\text{-}(CH_2)_n\text{-}X\text{-}CO\text{-}Y\text{-}(CH_2)_m\text{-}Si(R^2)_o(R^3)_{3-o}$$

with R^1 = H or CH_3; R^2 = independently selected from Cl, Br, O-C_{1-4} alkyl, O-C_{1-4} acyl; R^3 = independently selected from C_{1-4} alkyl; X = O; Y = NH; n = 6-12; m = 1-4; o = 1-3.

4. The dental composition according to any of the preceding claims, the surface-treating agent having a molecular weight Mw in the range of 300 to 800 g/mol.

5. The dental composition according to any of the preceding claims, the surface-treating agent being selected from the following molecules and mixtures thereof:



6. The dental composition according to any of the preceding claims, the filler comprising particles selected from non-aggregated and non-agglomerated nano-sized particles of SiO_2, ZrO_2 and mixtures thereof, aggregated nano-sized particles of SiO_2, ZrO_2 and mixtures thereof, agglomerated nano-sized particles of SiO_2, ZrO_2, Al_2O_3 and mixtures thereof, non acid-reactive particles of glasses, silicas, metal oxides or mixtures thereof, acid-reactive particles of glasses, metal oxides and hydroxide and mixtures thereof, and mixtures thereof,
wherein the individual particles of the nan-sized particles have an average particle diameter of less than 100 nm.

7. The dental composition according to any of the preceding claims comprising the surface-treated filler in an amount of 40 to 80 wt.% with respect to the weight of the dental composition.

8. The dental composition according to any of the preceding claims comprising the following components:
    a. surface-treated filler in an amount of 40 to 80 wt.%,
    b. curable components, particularly in an amount of 5 to 50 wt.%,
    c. initiator system suitable for curing the curable components, particularly in an amount of 0.1 to 5 wt.%,
    d. additives, particularly in an amount of 0 to 10 wt.%,

    wt.% with respect to the weight of the dental composition.

9. The dental composition according to any of the preceding claims, the dental composition comprising

    surface-treated filler in an amount of 40 to 80 wt.%, the filler particles being selected from non-aggregated, non-agglomerated nano-sized particles of SiO_2, ZrO_2 or mixtures thereof, aggregated nano-sized particles of SiO_2, ZrO_2, or mixtures thereof, agglomerated nano-sized particles of SiO_2, ZrO_2, Al_2O_3, or mixtures thereof, non acid-reactive particles of glasses, silicas, metal oxides or mixtures thereof, acid-reactive particles of glasses, metal oxides and hydroxide or mixtures thereof, wherein the individual particles of the nano-sized particles have an average particle diameter of less than 100 nm,

    curable components in an amount of 5 to 50 wt.%, the curable components being selected from polymerizable components comprising an acidic moiety, polymerizable components not comprising an acidic moiety, and mixtures thereof,

    initiator system in an amount of 0.1 to 5 wt.%, the initiator system being suitable for curing the curable components and comprising a photo-initiator system and/or redox-initiator system,

    additives in an amount of 0 to 10 wt.%,

    wt.% with respect to the weight of the dental composition,

    the surface-treating agent being characterized by the following features:

    comprising only one (meth)acrylate moiety,

    comprising at least one tri-methoxysilane or tri-ethoxysilane moiety,

    comprising only one urethane moiety,

    comprising one linear alkylene moiety AM1 connecting the (meth)acrylate moiety to the urethane moiety, the linear alkylene moiety AM1 comprising 6 to 12 C-atoms,

comprising one linear alkylene moiety AM2 connecting the at least one tri-methoxysilane or tri-ethoxysilane moiety with the urethane moiety, the linear alkylene moiety AM2 comprising 1 to 4 C-atoms.

10. The dental composition according to any of the preceding claims, the dental composition not comprising a rheological modifier, the dental composition being characterized by the following features alone or in combination before hardening:
    a. viscosity: 5 to 1,500 Pa*s at 25°C and a shear rate of 0.01 s^{-1};
    b. hardenable within 10 min after irradiation with light having a wavelength in the range of 400 to 700 nm;
    c. pH value: 7 or below.

11. The dental composition according to any of the preceding claims, the dental composition being characterized by the following features alone or in combination after hardening:
    a. flexural strength: 100 to 200 MPa determined according to ISO 4049 (2019);
    b. flexural modulus: 4 to 8 GPa determined according to ISO 4049 (2019).

12. A kit of parts comprising the dental composition according to any of the preceding claims and the following parts alone or in combination: a dental adhesive; a dental curing light; an application instrument.

13. A dental composition for use in a method of restoring a tooth in the mouth of a mammal, the dental composition being as described in any of claims 1 to 11, the method comprising the steps of

    bringing in contact the dental composition with the surface of the tooth to be restored,

    curing the dental composition by applying radiation.

14. A process for producing the dental composition according to any of claims 1 to 11, the process comprising the steps of

    combining the filler particles with the surface-treating agent, optionally using a dispersing liquid,

    reacting the surface-treating agent with the filler particles,

    removing the optional dispersing liquid,

optionally drying and sieving the surface-treated filler particles.

15. Use of the surface-treated filler as described in any of claims 1 to 11 for reducing the viscosity of a dental composition according to any of claims 1 to 11 at a low shear rate.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2023/061617

A. CLASSIFICATION OF SUBJECT MATTER

INV. A61K6/76 A61K6/77 A61K6/831 A61K6/836 C03C25/326
C03C25/40 C03C17/30 C03C17/32 C04B14/06 C04B14/22
C09C1/28 C09C3/10 C09C3/12

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)

A61K C03C C04B

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y A	JP 2017 014479 A (SUMITOMO OSAKA CEMENT CO LTD) 19 January 2017 (2017-01-19) paragraphs [0110] - [0116]; example 8; tables 3,4	1,4,6,14 2 3,5
Y A	US 6 277 502 B1 (BUCHECKER RICHARD [CH] ET AL) 21 August 2001 (2001-08-21) column 13, line 42 - column 14, line 61; example 4	2 1,3-6,14
X	US 6 730 156 B1 (WINDISCH MARK STEVEN [US] ET AL) 4 May 2004 (2004-05-04) cited in the application column 27, line 10 - column 29, line 50; tables 1-6	7-13,15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 February 2024	15/02/2024

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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