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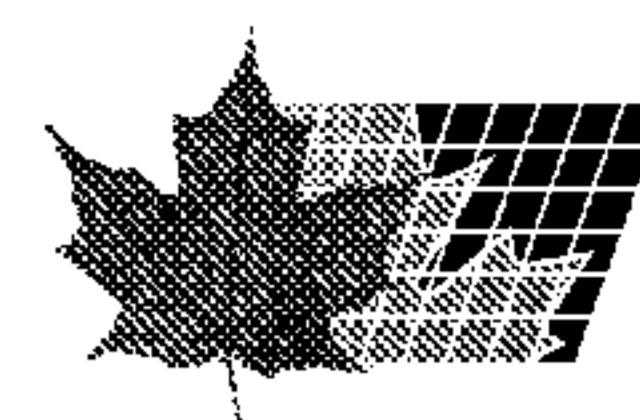
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(54) Title: DENTAL FILLERS INCLUDING A PHOSPHORUS CONTAINING SURFACE TREATMENT, AND COMPOSITIONS AND METHODS THEREOF

(57) **Abrégé/Abstract:**

The present application provides dental fillers, and methods of making and using dental fillers that include a treated surface that includes phosphorus and a divalent cation. Dental compositions including such dental fillers can be useful for delivering ions to the oral environment.



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(54) Title: DENTAL FILLERS INCLUDING A PHOSPHORUS CONTAINING SURFACE TREATMENT, AND COMPOSITIONS AND METHODS THEREOF

(57) Abstract: The present application provides dental fillers, and methods of making and using dental fillers that include a treated surface that includes phosphorus and a divalent cation. Dental compositions including such dental fillers can be useful for delivering ions to the oral environment.

# DENTAL FILLERS INCLUDING A PHOSPHORUS-CONTAINING SURFACE TREATMENT, AND COMPOSITIONS AND METHODS THEREOF

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## BACKGROUND

Demineralization of dental structures is well known to lead to caries, decayed dentin, cementum, and/or enamel, conditions that typically require treatment with a dental restorative, for example. Although such conditions can usually be adequately treated using dental restoratives, restored dental structures oftentimes can be susceptible to further decay around the margins of the restoration.

The release of ions (e.g., calcium, and preferably calcium and phosphorus) into the oral environment is known to enhance the natural remineralizing capability of dental structures. It is believed that enhanced remineralization may be a useful supplement to, or even an alternative to, traditional dental restorative methods. However, known compositions that release calcium and phosphorus into the oral environment (e.g., calcium phosphate containing compositions) oftentimes lack desirable properties including, for example, sustained release capabilities.

20 Thus, new compositions capable of releasing ions (e.g., phosphorus and other ions) into the oral environment are needed.

## SUMMARY OF THE INVENTION

The present invention provides a dental filler including a treated surface, and methods of preparing such a dental filler including a treated surface. The treated surface includes phosphorus and a divalent cation selected from the group consisting of Mg, Ca, Sr, Ba, Zn, and combinations thereof. Dental compositions including such a dental filler, and methods of using such dental compositions are also provided.

Dental fillers and compositions as disclosed herein preferably lead to enhanced 30 remineralization of dental structures, which can offer potential benefits including, for example, the ability to remineralize enamel and/or dentin lesions; to occlude exposed

dentin and/or cementum tubules which cause sensitivity; to recondition abraded and/or etched enamel surfaces; to reseal microleakage regions at interfaces; and to increase resistance of contacted and nearby tooth structures to acid attack.

## 5 *Definitions*

As used herein, "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 the dental structure. An "orthodontic adhesive" refers to a highly (generally greater than 40 % by weight) filled composition (more analogous to a "restorative material" than to a "dental adhesive") used to adhere an orthodontic appliance to a dental structure (e.g., tooth) surface. Generally, the dental structure 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 structure surface.

15 As used herein, a "non-aqueous" composition (e.g., an adhesive) refers to a composition in which water has not been added as a component. However, there may be adventitious water in other components of the composition, but the total amount of water does not adversely affect stability (e.g., the shelf-life) of the non-aqueous composition. Non-aqueous compositions preferably include less than 1% by weight, more preferably 20 less than 0.5% by weight, and most preferably less than 0.1% by weight water, based on the total weight of the non-aqueous composition.

25 As used herein, a "self-etching" composition refers to a composition that bonds to a dental structure surface without pretreating the dental structure surface with an etchant. Preferably, a self-etching composition can also function as a self-primer wherein no separate etchant or primer are used.

As used herein, a "self-adhesive" composition refers to a composition that is capable of bonding to a dental structure surface without pretreating the dental structure surface with a primer or bonding agent. Preferably, a self-adhesive composition is also a self-etching composition wherein no separate etchant is used.

30 As used herein, "hardening" or "curing" a composition are used interchangeably and refer to polymerization and/or crosslinking reactions including, for example, photopolymerization reactions and chemical polymerization techniques (e.g., ionic

reactions (reactions or chemical reactions forming radicals effective to polymerize ethylenically unsaturated compounds) involving one or more compounds capable of hardening or curing.

As used herein, a "dental structure surface" refers to tooth structures (e.g., enamel, 5 dentin, and cementum) and bone.

As used herein, "dental material" refers to a material that may be bonded to a dental structure surface and includes, for example, dental restoratives, orthodontic appliances, and/or orthodontic adhesives.

As used herein, "(meth)acryl" is a shorthand term referring to "acryl" and/or 10 "methacryl." For example, a "(meth)acryloxy" group is a shorthand term referring to either an acryloxy group (i.e.,  $\text{CH}_2=\text{CHC}(\text{O})\text{O}-$ ) and/or a methacryloxy group (i.e.,  $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{O}-$ ).

As used herein, an "amorphous" material is one which does not give rise to a discernible x-ray powder diffraction pattern. An "at least partially crystalline" material is 15 one which gives rise to a discernible x-ray powder diffraction pattern.

As used herein, "groups" of the periodic table refer to and include groups 1-18 as defined in IUPAC Nomenclature of Inorganic Chemistry, Recommendations 1990.

As used herein, "a" or "an" means "at least one" or "one or more" unless otherwise indicated.

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## DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention provides dental fillers and/or compositions that include phosphorus and a divalent cation. In some embodiments, a dental filler is provided that includes a treated surface that includes phosphorus and a divalent cation. In some 25 embodiments, dental compositions are provided that include such dental fillers. In some embodiments, dental compositions are provided that include phosphorus and a divalent cation, and a hardenable resin and/or a water-dispersible, polymeric film former. Methods of making and using such dental fillers and/or compositions are also provided.

### 30 PHOSPHORUS AND DIVALENT CATION PRECURSORS

Phosphorus precursors and divalent cation precursors can be used to surface treat dental fillers. Phosphorus precursors can be the same as or different than divalent cation

precursors. Preferably, the divalent cation precursor includes Mg, Ca, Sr, Ba, Zn, or a combination thereof as divalent cation.

Suitable precursors for phosphorus include, for example, phosphoric acid and salts thereof (e.g., sodium phosphate, potassium phosphate, calcium phosphate, magnesium phosphate, etc.), pyrophosphoric acid and salts thereof (e.g., tetrasodium pyrophosphate, calcium pyrophosphate), monofluorophosphoric acid and salts thereof, hexafluorophosphoric acid and salts thereof, phosphate esters (e.g., triethylphosphate), glycerophosphates (e.g., calcium glycerophosphate, zinc glycerophosphate, magnesium glycerophosphate, strontium glycerophosphate, tin glycerophosphate, zirconium glycerophosphate, and silver glycerophosphate), caseinates (e.g., calcium phosphate complexed caseinates), phosphorous oxides (e.g.,  $P_2O_5$ ), phosphorus oxyhalides (e.g.,  $POCl_3$ ), and combinations thereof.

Suitable precursors for divalent cations include organic and inorganic salts of the cation with an anion, and basic or oxy salts thereof. Exemplary anions include, for example, nitrate, halide (e.g., chloride, fluoride, etc.), hydroxide, alkoxide, caseinate, carboxylate (e.g., formate, acetate, formoacetate), and combinations thereof.

In addition, precursors for other cations (e.g., trivalent cations) and/or anions (e.g., fluoride ion) may optionally be used to surface treat the dental fillers.

For example, suitable precursors for trivalent cations (e.g., aluminum, lanthanum, or combinations thereof) include, for organic and inorganic salts of the cation with an anion, and basic or oxy salts thereof. Exemplary anions include, for example, nitrate, halide (e.g., chloride, fluoride, etc.), hydroxide, alkoxide, caseinate, carboxylate (e.g., formate, acetate, formoacetate), and combinations thereof.

Further, suitable precursors for fluoride ion include, for example, ammonium fluoride, ammonium hydrogen difluoride, hexafluorosilicic acid and salts thereof, monofluorophosphoric acid and salts thereof, hexafluorophosphoric acid and salts thereof, and combinations thereof.

#### *SURFACE TREATMENT OF DENTAL FILLERS*

30 Preferably, the dental fillers are surface treated by methods similar to those described, for example, in U.S. Pat. No. 5,332,429 (Mitra et al.). In brief, the dental fillers described herein can be surface treated by combining the filler with one or more liquids

having dissolved, dispersed, or suspended therein, a phosphorus precursor and a divalent cation precursor as described herein. The one or more liquids or additional liquids may optionally include additional surface treating agents (e.g., fluoride ion precursors, silanes, titanates, etc). Optionally the one or more liquids include water, and if an aqueous liquid is used, it can be acidic or basic. Once treated, at least a portion of the one or more liquids can be removed from the surface treated dental filler using any convenient technique (e.g., spray drying, oven drying, gap drying, lyophilizing, and combinations thereof). See, for example, U.S. Pat. No. 5,980,697 (Kolb et al.) for a description of gap drying. In one embodiment, the treated fillers can be oven dried, typically at drying temperatures of about 5 30° to about 100°C, for example, overnight. The surface treated filler can be further heated as desired. The treated and dried dental filler can then be screened or lightly comminuted to break up agglomerates. The resulting surface treated dental filler can be 10 incorporated, for example, into a dental paste.

Dental fillers suitable for surface treatment can be selected from one or more of a 15 wide variety of materials suitable for incorporation in compositions used for dental applications, such as fillers currently used in dental restorative compositions, and the like. Preferably the dental filler includes porous particles and/or porous agglomerates of particles. Preferred dental fillers include nanoparticles and/or agglomerates of nanoparticles. Preferred classes of fillers include metal oxides, metal fluorides, metal 20 oxyfluorides, and combinations thereof, wherein the metal can be a heavy or non-heavy metal.

In preferred embodiments, the dental filler is an oxide, a fluoride, or an oxyfluoride of an element selected from the group consisting of Groups 2-5 elements, Groups 12-15 elements, Lanthanide elements, and combinations thereof. More preferably, the element is 25 selected from the group consisting of Ca, Sr, Ba, Y, La, Ce, Pr, Nd, Pm, Sm Eu, Gd, Tb, Dy, Ho, Er, Tm Yb, Lu, Ti, Zr, Ta, Zn B, Al, Si, Sn, P, and combinations thereof. The dental filler can be a glass, an amorphous material, or a crystalline material. Optionally, the dental filler can include a source of fluoride ions. Such dental fillers include, for example, fluoroaluminosilicate glasses.

30 The filler is preferably finely divided. The filler can have a unimodal or polymodal (e.g., bimodal) particle size distribution. Preferably, the maximum particle size (the largest dimension of a particle, typically, the diameter) of the filler is less than 20

micrometers, more preferably less than 10 micrometers, and most preferably less than 5 micrometers. Preferably, the average particle size of the filler is less than 2 micrometers, more preferably less than 0.1 micrometers, and most preferably less than 0.075 micrometer.

5 The filler can be an inorganic material. It can also be a crosslinked organic material that is insoluble in the resin system, and is optionally filled with inorganic filler. The filler should in any event be nontoxic and suitable for use in the mouth. The filler can be radiopaque or radiolucent. The filler typically is substantially insoluble in water.

10 Examples of suitable inorganic fillers are naturally occurring or synthetic materials including, but not limited to: quartz; nitrides (e.g., silicon nitride); glasses derived from, for example, Zr, Sr, Ce, Sb, Sn, Ba, Zn, and Al; feldspar; borosilicate glass; kaolin; talc; titania; low Mohs hardness fillers such as those described in U.S. Pat. No. 4,695,251 (Randklev); and submicron silica particles (e.g., pyrogenic silicas such as those available under the trade designations AEROSIL, including "OX 50," "130," "150" and "200" silicas 15 from Degussa Corp., Akron, OH and CAB-O-SIL M5 silica from Cabot Corp., Tuscola, IL). Examples of suitable organic filler particles include filled or unfilled pulverized polycarbonates, polyepoxides, and the like.

Preferred non-acid-reactive filler particles are quartz, submicron silica, and non-vitreous microparticles of the type described in U.S. Pat. No. 4,503,169 (Randklev). 20 Mixtures of these non-acid-reactive fillers are also contemplated, as well as combination fillers made from organic and inorganic materials. Silane-treated zirconia-silica (Zr-Si) filler is especially preferred in certain embodiments.

The filler can also be an acid-reactive filler. Suitable acid-reactive fillers include metal oxides, glasses, and metal salts. Typical metal oxides include barium oxide, calcium 25 oxide, magnesium oxide, and zinc oxide. Typical glasses include borate glasses, phosphate glasses, and fluoroaluminosilicate ("FAS") glasses. FAS glasses are particularly preferred. The FAS glass typically contains sufficient elutable cations so that a hardened dental composition will form when the glass is mixed with the components of the hardenable composition. The glass also typically contains sufficient elutable fluoride 30 ions so that the hardened composition will have cariostatic properties. The glass can be made from a melt containing fluoride, alumina, and other glass-forming ingredients using techniques familiar to those skilled in the FAS glassmaking art. The FAS glass typically

is in the form of particles that are sufficiently finely divided so that they can conveniently be mixed with the other cement components and will perform well when the resulting mixture is used in the mouth.

Generally, the average particle size (typically, diameter) for the FAS glass is no 5 greater than about 12 micrometers, typically no greater than 10 micrometers, and more typically no greater than 5 micrometers as measured using, for example, a sedimentation analyzer. Suitable FAS glasses will be familiar to those skilled in the art, and are available from a wide variety of commercial sources, and many are found in currently available glass ionomer cements such as those commercially available under the trade designations 10 VITREMER, VITREBOND, RELY X LUTING CEMENT, RELY X LUTING PLUS CEMENT, PHOTAC-FIL QUICK, KETAC-MOLAR, and KETAC-FIL PLUS (3M ESPE Dental Products, St. Paul, MN), FUJI II LC and FUJI IX (G-C Dental Industrial Corp., Tokyo, Japan) and CHEMFIL Superior (Dentsply International, York, PA). Mixtures of fillers can be used if desired.

15 Other suitable fillers are disclosed, for example, in U.S. Pat. Nos. 6,306,926 (Bretscher et al.), 6,387,981 (Zhang et al.), 6,572,693 (Wu et al.), and 6,730,156 (Windisch et al.), as well as International Publication Nos. WO 01/30307 (Zhang et al.) and WO 03/063804 (Wu et al.). Filler components described in these references include nanosized silica particles, nanosized metal oxide particles, and combinations thereof. 20 Nanofillers are also described in U.S. Patent Application Serial Nos. 10/847,781; 10/847,782; and 10/847,803; all three of which were filed on May 17, 2004.

The surface treated dental filler preferably includes at least 0.01%, more preferably at least 0.05%, and most preferably at least 0.1% by weight phosphorus, based on the total dry weight of the dental filler (i.e., excluding the liquid used in the treatment). The 25 surface treated dental filler preferably includes at most 50%, more preferably at most 30%, and most preferably at most 20% by weight phosphorus, based on the total dry weight of the dental filler (i.e., excluding the liquid used in the treatment).

The surface treated dental filler preferably includes at least 0.01%, more preferably at least 0.05%, and most preferably at least 0.1% by weight divalent cation, based on the 30 total dry weight of the dental filler (i.e., excluding the liquid used in the treatment). The surface treated dental filler preferably includes at most 50%, more preferably at most 30%,

and most preferably at most 20% by weight divalent cation, based on the total dry weight of the dental filler (i.e., excluding the liquid used in the treatment).

For some embodiments of the present invention that include surface treated dental filler (e.g., dental adhesive compositions), the compositions preferably include at least 1% by weight, more preferably at least 2% by weight, and most preferably at least 5% by weight surface treated dental filler, based on the total weight of the composition. For such embodiments, compositions of the present invention preferably include at most 40% by weight, more preferably at most 20% by weight, and most preferably at most 15% by weight surface treated dental filler, based on the total weight of the composition.

For other embodiments (e.g., wherein the composition is a dental restorative or an orthodontic adhesive), compositions of the present invention preferably include at least 40% by weight, more preferably at least 45% by weight, and most preferably at least 50% by weight surface treated dental filler, based on the total weight of the composition. For such embodiments, compositions of the present invention preferably include at most 90% by weight, more preferably at most 80% by weight, even more preferably at most 70% by weight, and most preferably at most 50% by weight surface treated dental filler, based on the total weight of the composition.

Optionally, the treated surface of the dental filler can further include a silane (e.g., as described, for example, in U.S. Pat. No. 5,332,429 (Mitra et al.)), an antibacterial agent (e.g., chlorhexidine; quaternary ammonium salts; metal containing compounds such as Ag, Sn, or Zn containing compounds; and combinations thereof), and/or a source of fluoride ions (e.g., fluoride salts, fluoride containing glasses, fluoride containing compounds, and combinations thereof).

Dental compositions of the present invention can also include optional additives as described herein below.

Dental compositions as described herein can be useful as dental primers, dental adhesives, cavity liners, cavity cleansing agents, cements, coatings, varnishes, orthodontic adhesives, restoratives, sealants, desensitizers, and combinations thereof.

Dental compositions of the present invention are useful for treating hard surfaces, preferably, hard tissues such as dentin, enamel, and bone. Such dental compositions can be aqueous or non-aqueous. In some embodiments, the compositions can be hardened (e.g., polymerized by conventional photopolymerization and/or chemical polymerization techniques) prior to applying the dental material. In other embodiments, the compositions can be hardened (e.g., polymerized by conventional photopolymerization and/or chemical polymerization techniques) after applying the dental material.

Suitable photopolymerizable compositions that can be used as dental materials and dental adhesive compositions in methods of the present invention can include epoxy resins (which contain cationically active epoxy groups), vinyl ether resins (which contain cationically active vinyl ether groups), ethylenically unsaturated compounds (which contain free radically active unsaturated groups, e.g., acrylates and methacrylates), and combinations thereof. Also suitable are polymerizable materials that contain both a cationically active functional group and a free radically active functional group in a single compound. Examples include epoxy-functional (meth)acrylates.

#### *ETHYLENICALLY UNSATURATED COMPOUNDS WITH ACID FUNCTIONALITY*

As used herein, ethylenically unsaturated compounds with acid functionality is meant to include monomers, oligomers, and polymers having ethylenic unsaturation and acid and/or acid-precursor functionality. Acid-precursor functionalities include, for example, anhydrides, acid halides, and pyrophosphates.

Ethylenically unsaturated compounds with acid functionality include, for example,  $\alpha,\beta$ -unsaturated acidic compounds such as glycerol phosphate mono(meth)acrylates, glycerol phosphate di(meth)acrylates, hydroxyethyl (meth)acrylate (e.g., HEMA) phosphates, bis((meth)acryloxyethyl) phosphate, ((meth)acryloxypropyl) phosphate, bis((meth)acryloxypropyl) phosphate, bis((meth)acryloxy)propoxy 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-methacrylates, 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, may be used as components in the hardenable resin system. Also monomers, oligomers, and polymers of unsaturated carbonic acids such as (meth)acrylic acids, aromatic (meth)acrylated acids (e.g., methacrylated trimellitic acids), and anhydrides thereof can be 5 used. Certain preferred compositions of the present invention include an ethylenically unsaturated compound with acid functionality having at least one P-OH moiety.

Certain of these compounds are obtained, for example, as reaction products between isocyanatoalkyl (meth)acrylates and carboxylic acids. Additional compounds of this type having both acid-functional and ethylenically unsaturated components are 10 described in U.S. Pat. Nos. 4,872,936 (Engelbrecht) and 5,130,347 (Mitra). A wide variety of such compounds containing both the ethylenically unsaturated and acid moieties can be used. Mixtures of such compounds can be used if desired.

Additional ethylenically unsaturated compounds with acid functionality include, for example, polymerizable bisphosphonic acids as disclosed for example, in U.S. 15 Provisional Application No. 60/437,106, filed December 30, 2002; AA:ITA:IEM (copolymer of acrylic acid:itaconic acid with pendent methacrylate made by reacting AA:ITA copolymer with sufficient 2-isocyanatoethyl methacrylate to convert a portion of the acid groups of the copolymer to pendent methacrylate groups as described, for example, in Example 11 of U.S. Pat. No. 5,130,347 (Mitra)); and those recited in U.S. Pat. 20 Nos. 4,259,075 (Yamauchi et al.), 4,499,251 (Omura et al.), 4,537,940 (Omura et al.), 4,539,382 (Omura et al.), 5,530,038 (Yamamoto et al.), 6,458,868 (Okada et al.), and European Pat. Application Publication Nos . EP 712,622 (Tokuyama Corp.) and EP 1,051,961 (Kuraray Co., Ltd.).

Compositions of the present invention can also include combinations of 25 ethylenically unsaturated compounds with acid functionality as described, for example, in U.S. Provisional Application Serial No. 60/600,658, filed on August 11, 2004.

Preferably, the compositions of the present invention include at least 1% by weight, more preferably at least 3% by weight, and most preferably at least 5% by weight ethylenically unsaturated compounds with acid functionality, based on the total weight of 30 the unfilled composition. Preferably, compositions of the present invention include at most 80% by weight, more preferably at most 70% by weight, and most preferably at most

60% by weight ethylenically unsaturated compounds with acid functionality, based on the total weight of the unfilled composition.

#### *ETHYLENICALLY UNSATURATED COMPOUNDS WITHOUT ACID FUNCTIONALITY*

5 The compositions of the present invention may also include one or more polymerizable components in addition to the ethylenically unsaturated compounds with acid functionality, thereby forming hardenable compositions. The polymerizable components may be monomers, oligomers, or polymers.

10 In certain embodiments, the compositions are photopolymerizable, i.e., the compositions contain a photopolymerizable component and a photoinitiator (i.e., a photoinitiator system) that upon irradiation with actinic radiation initiates the polymerization (or hardening) of the composition. Such photopolymerizable compositions can be free radically polymerizable.

15 In certain embodiments, the compositions are chemically polymerizable, i.e., the compositions contain a chemically polymerizable component and a chemical initiator (i.e., initiator system) that can polymerize, cure, or otherwise harden the composition without dependence on irradiation with actinic radiation. Such chemically polymerizable compositions are sometimes referred to as "self-cure" compositions and may include glass ionomer cements, resin-modified glass ionomer cements, redox cure systems, and 20 combinations thereof.

25 Preferably, compositions of the present invention include at least 5% by weight, more preferably at least 10% by weight, and most preferably at least 15% by weight ethylenically unsaturated compounds without acid functionality, based on the total weight of the unfilled composition. Preferably, compositions of the present invention include at most 95% by weight, more preferably at most 90% by weight, and most preferably at most 80% by weight ethylenically unsaturated compounds without acid functionality, based on the total weight of the unfilled composition.

#### *Photopolymerizable Compositions*

30 Suitable photopolymerizable compositions may include photopolymerizable components (e.g., compounds) that include ethylenically unsaturated compounds (which contain free radically active unsaturated groups). Examples of useful ethylenically

unsaturated compounds include acrylic acid esters, methacrylic acid esters, hydroxy-functional acrylic acid esters, hydroxy-functional methacrylic acid esters, and combinations thereof.

Photopolymerizable compositions may include compounds having free radically active functional groups that may include monomers, oligomers, and polymers having one or more ethylenically unsaturated group. Suitable compounds contain at least one ethylenically unsaturated bond and are capable of undergoing addition polymerization. Such free radically polymerizable compounds include mono-, di- or poly-(meth)acrylates (i.e., acrylates and methacrylates) such as, methyl (meth)acrylate, ethyl acrylate, isopropyl 10 methacrylate, n-hexyl acrylate, stearyl acrylate, allyl acrylate, glycerol triacrylate, ethyleneglycol diacrylate, diethyleneglycol diacrylate, triethyleneglycol dimethacrylate, 1,3-propanediol di(meth)acrylate, trimethylolpropane triacrylate, 1,2,4-butanetriol trimethacrylate, 1,4-cyclohexanediol diacrylate, pentaerythritol tetra(meth)acrylate, sorbitol hexacrylate, tetrahydrofurfuryl (meth)acrylate, bis[1-(2-acryloxy)]-p- 15 ethoxyphenyldimethylmethane, bis[1-(3-acryloxy-2-hydroxy)]-p-propoxyphenyldimethylmethane, ethoxylated bisphenolA di(meth)acrylate, and trishydroxyethyl-isocyanurate trimethacrylate; (meth)acrylamides (i.e., acrylamides and methacrylamides) such as (meth)acrylamide, methylene bis-(meth)acrylamide, and diacetone (meth)acrylamide; urethane (meth)acrylates; the bis-(meth)acrylates of 20 polyethylene glycols (preferably of molecular weight 200-500), copolymerizable mixtures of acrylated monomers such as those in U.S. Pat. No. 4,652,274 (Boettcher et al.), acrylated oligomers such as those of U.S. Pat. No. 4,642,126 (Zador et al.), and poly(ethylenically unsaturated) carbamoyl isocyanurates such as those disclosed in U.S. Pat. No. 4,648,843 (Mitra); and vinyl compounds such as styrene, diallyl phthalate, divinyl 25 succinate, divinyl adipate and divinyl phthalate. Other suitable free radically polymerizable compounds include siloxane-functional (meth)acrylates as disclosed, for example, in WO-00/38619 (Guggenberger et al.), WO-01/92271 (Weinmann et al.), WO-01/07444 (Guggenberger et al.), WO-00/42092 (Guggenberger et al.) and fluoropolymer-functional (meth)acrylates as disclosed, for example, in U.S. Pat. No. 5,076,844 (Fock et al.), U.S. Pat. No. 4,356,296 (Griffith et al.), EP-0373 384 (Wagenknecht et al.), EP-0201 30 031 (Reiners et al.), and EP-0201 778 (Reiners et al.). Mixtures of two or more free radically polymerizable compounds can be used if desired.

The polymerizable component may also contain hydroxyl groups and free radically active functional groups in a single molecule. Examples of such materials include hydroxyalkyl (meth)acrylates, such as 2-hydroxyethyl (meth)acrylate and 2-hydroxypropyl (meth)acrylate; glycerol mono- or di-(meth)acrylate; trimethylolpropane mono- or di-(meth)acrylate; pentaerythritol mono-, di-, and tri-(meth)acrylate; sorbitol mono-, di-, tri-, tetra-, or penta-(meth)acrylate; and 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane (bisGMA). Suitable ethylenically unsaturated compounds are also available from a wide variety of commercial sources, such as Sigma-Aldrich, St. Louis. Mixtures of ethylenically unsaturated compounds can be used if desired.

In certain embodiments photopolymerizable components include PEGDMA (polyethyleneglycol dimethacrylate having a molecular weight of approximately 400), bisGMA, UDMA (urethane dimethacrylate), GDMA (glycerol dimethacrylate), TEGDMA (triethyleneglycol dimethacrylate), bisEMA6 as described in U.S. Pat. No. 6,030,606 (Holmes), and NPGDMA (neopentylglycol dimethacrylate). Various combinations of the polymerizable components can be used if desired.

Suitable photoinitiators (i.e., photoinitiator systems that include one or more compounds) for polymerizing free radically photopolymerizable compositions include binary and tertiary systems. Typical tertiary photoinitiators include an iodonium salt, a photosensitizer, and an electron donor compound as described in U.S. Pat. No. 5,545,676 (Palazzotto et al.). Preferred iodonium salts are the diaryl iodonium salts, e.g., diphenyliodonium chloride, diphenyliodonium hexafluorophosphate, diphenyliodonium tetrafluoroborate, and tolylcumyliodonium tetrakis(pentafluorophenyl)borate. Preferred photosensitizers are monoketones and diketones that absorb some light within a range of 400 nm to 520 nm (preferably, 450 nm to 500 nm). More preferred compounds are alpha diketones that have some light absorption within a range of 400 nm to 520 nm (even more preferably, 450 to 500 nm). Preferred compounds are camphorquinone, benzil, furil, 3,3,6,6-tetramethylcyclohexanedione, phenanthraquinone, 1-phenyl-1,2-propanedione and other 1-aryl-2-alkyl-1,2-ethanediiones, and cyclic alpha diketones. Most preferred is camphorquinone. Preferred electron donor compounds include substituted amines, e.g., ethyl dimethylaminobenzoate. Other suitable tertiary photoinitiator systems useful for

photopolymerizing cationically polymerizable resins are described, for example, in U.S. Pat. Publication No. 2003/0166737 (Dede et al.).

Other suitable photoinitiators for polymerizing free radically photopolymerizable compositions include the class of phosphine oxides that typically have a functional wavelength range of 380 nm to 1200 nm. Preferred phosphine oxide free radical initiators with a functional wavelength range of 380 nm to 450 nm are acyl and bisacyl phosphine oxides such as those described in U.S. Pat. Nos. 4,298,738 (Lechtken et al.), 4,324,744 (Lechtken et al.), 4,385,109 (Lechtken et al.), 4,710,523 (Lechtken et al.), and 4,737,593 (Ellrich et al.), 6,251,963 (Kohler et al.); and EP Application No. 0 173 567 A2 (Ying).

Commercially available phosphine oxide photoinitiators capable of free-radical initiation when irradiated at wavelength ranges of greater than 380 nm to 450 nm include bis(2,4,6-trimethylbenzoyl)phenyl phosphine oxide (IRGACURE 819, Ciba Specialty Chemicals, Tarrytown, NY), bis(2,6-dimethoxybenzoyl)-(2,4,4-trimethylpentyl) phosphine oxide (CGI 403, Ciba Specialty Chemicals), 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 (IRGACURE 1700, Ciba Specialty Chemicals), a 1:1 mixture, by weight, of bis(2,4,6-trimethylbenzoyl)phenyl phosphine oxide and 2-hydroxy-2-methyl-1-phenylpropane-1-one (DAROCUR 4265, Ciba Specialty Chemicals), and ethyl 2,4,6-trimethylbenzylphenyl phosphinate (LUCIRIN LR8893X, BASF Corp., Charlotte, NC).

Typically, the phosphine oxide initiator is present in the photopolymerizable composition in catalytically effective amounts, such as from 0.1 weight percent to 5.0 weight percent, based on the total weight of the composition.

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. When present, the amine reducing agent is present in the photopolymerizable composition in an amount from 0.1 weight percent to 5.0 weight percent, based on the total weight of the composition.

Useful amounts of other initiators are well known to those of skill in the art.

30

*Chemically Polymerizable Compositions*

The chemically polymerizable compositions may include redox cure systems that include a polymerizable component (e.g., an ethylenically unsaturated polymerizable component) and redox agents that include an oxidizing agent and a reducing agent. Suitable polymerizable components, redox agents, optional acid-functional components, 5 and optional fillers that are useful in the present invention are described in U.S. Pat. Publication Nos. 2003/0166740 (Mitra et al.) and 2003/0195273 (Mitra et al.).

The reducing and oxidizing agents should react with or otherwise cooperate with one another to produce free-radicals capable of initiating polymerization of the resin system (e.g., the ethylenically unsaturated component). This type of cure is a dark 10 reaction, that is, it is not dependent on the presence of light and can proceed in the absence of light. The reducing and oxidizing agents are preferably sufficiently shelf-stable and free of undesirable colorization to permit their storage and use under typical dental conditions. They should be sufficiently miscible with the resin system (and preferably water-soluble) to permit ready dissolution in (and discourage separation from) the other 15 components of the polymerizable composition.

Useful reducing agents include ascorbic acid, ascorbic acid derivatives, and metal complexed ascorbic acid compounds as described in U.S. Pat. No. 5,501,727 (Wang et al.); amines, especially tertiary amines, such as 4-tert-butyl dimethylaniline; aromatic sulfinic salts, such as p-toluenesulfinic salts and benzenesulfinic salts; thioureas, such as 20 1-ethyl-2-thiourea, tetraethyl thiourea, tetramethyl thiourea, 1,1-dibutyl thiourea, and 1,3-dibutyl thiourea; and mixtures thereof. Other secondary reducing agents may include cobalt (II) chloride, ferrous chloride, ferrous sulfate, hydrazine, hydroxylamine (depending on the choice of oxidizing agent), salts of a dithionite or sulfite anion, and mixtures thereof. Preferably, the reducing agent is an amine.

25 Suitable oxidizing agents will also be familiar to those skilled in the art, and include but are not limited to persulfuric acid and salts thereof, such as sodium, potassium, ammonium, cesium, and alkyl ammonium salts. Additional oxidizing agents include peroxides such as benzoyl peroxides, hydroperoxides such as cumyl hydroperoxide, t-butyl hydroperoxide, and amyl hydroperoxide, as well as salts of transition metals such as 30 cobalt (III) chloride and ferric chloride, cerium (IV) sulfate, perboric acid and salts thereof, permanganic acid and salts thereof, perchloric acid and salts thereof, and mixtures thereof.

It may be desirable to use more than one oxidizing agent or more than one reducing agent. Small quantities of transition metal compounds may also be added to accelerate the rate of redox cure. In some embodiments it may be preferred to include a secondary ionic salt to enhance the stability of the polymerizable composition as described 5 in U.S. Pat. Publication No. 2003/0195273 (Mitra et al.).

The reducing and oxidizing agents are present in amounts sufficient to permit an adequate free-radical reaction rate. This can be evaluated by combining all of the ingredients of the polymerizable composition except for the optional filler, and observing whether or not a hardened mass is obtained.

10 Preferably, the reducing agent is present in an amount of at least 0.01% by weight, and more preferably at least 0.1% by weight, based on the total weight (including water) of the components of the polymerizable composition. Preferably, the reducing agent is present in an amount of no greater than 10% by weight, and more preferably no greater than 5% by weight, based on the total weight (including water) of the components of the 15 polymerizable composition.

Preferably, the oxidizing agent is present in an amount of at least 0.01% by weight, and more preferably at least 0.10% by weight, based on the total weight (including water) of the components of the polymerizable composition. Preferably, the oxidizing agent is present in an amount of no greater than 10% by weight, and more preferably no greater 20 than 5% by weight, based on the total weight (including water) of the components of the polymerizable composition.

25 The reducing or oxidizing agents can be microencapsulated as described in U.S. Pat. No. 5,154,762 (Mitra et al.). This will generally enhance shelf stability of the polymerizable composition, and if necessary permit packaging the reducing and oxidizing agents together. For example, through appropriate selection of an encapsulant, the oxidizing and reducing agents can be combined with an acid-functional component and optional filler and kept in a storage-stable state. Likewise, through appropriate selection of a water-insoluble encapsulant, the reducing and oxidizing agents can be combined with an FAS glass and water and maintained in a storage-stable state.

30 A redox cure system can be combined with other cure systems, e.g., with a photopolymerizable composition such as described U.S. Pat. No. 5,154,762 (Mitra et al.).

In some embodiments, dental compositions of the present invention including a hardenable resin can be hardened to fabricate a dental article selected from the group consisting of crowns, fillings, mill blanks, orthodontic devices, and prostheses.

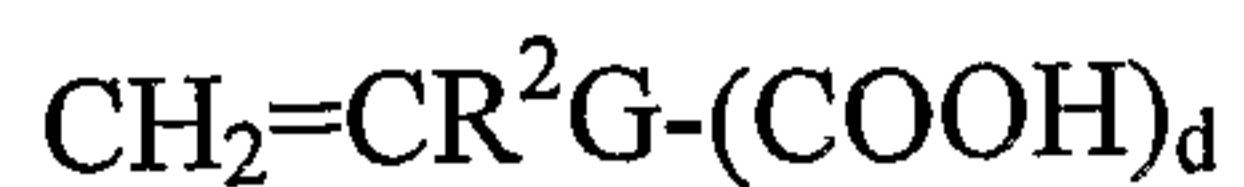
## 5 *WATER-DISPERSIBLE POLYMERIC FILM FORMER*

In some embodiments, water-dispersible polymeric film formers as disclosed herein include a repeating unit that includes a polar or polarizable group as described herein below. In certain embodiments, the water-dispersible polymeric film formers also include a repeating unit that includes a fluoride releasing group, a repeating unit that includes a hydrophobic hydrocarbon group, a repeating unit that includes a graft polysiloxane chain, a repeating unit that includes a hydrophobic fluorine-containing group, a repeating unit that includes a modulating group, or combinations thereof, as described herein below. In some embodiments, the polymer optionally includes a reactive group (e.g., ethylenically unsaturated groups, epoxy groups, or silane moieties capable of undergoing a condensation reaction). Exemplary water-dispersible polymeric film formers are disclosed, for example, in U.S. Pat. Nos. 5,468,477 (Kumar et al.), 5,525,648 (Aasen et al.), 5,607,663 (Rozzi et al.), 5,662,887 (Rozzi et al.), 5,725,882 (Kumar et al.), 5,866,630 (Mitra et al.), 5,876,208 (Mitra et al.), 5,888,491 (Mitra et al.), and 6,312,668 (Mitra et al.).

20 Repeating units including a polar or polarizable group are derived from vinylic monomers such as acrylates, methacrylates, crotonates, itaconates, and the like. The polar groups can be acidic, basic or salt. These groups can also be ionic or neutral.

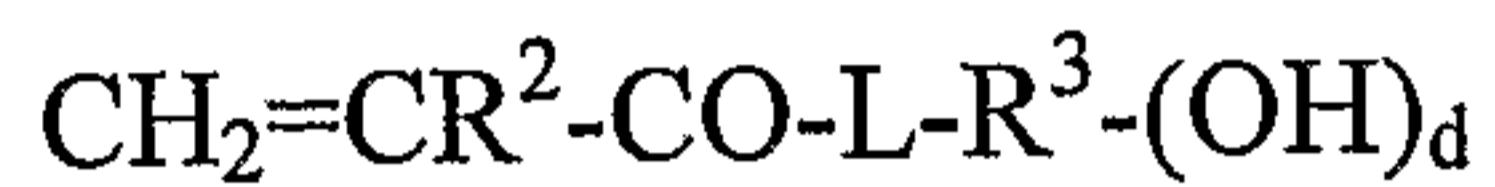
25 Examples of polar or polarizable groups include neutral groups such as hydroxy, thio, substituted and unsubstituted amido, cyclic ethers (such as oxanes, oxetanes, furans and pyrans), basic groups (such as phosphines and amines, including primary, secondary, tertiary amines), acidic groups (such as oxy acids, and thiooxyacids of C, S, P, B), ionic groups (such as quarternary ammonium, carboxylate salt, sulfonic acid salt and the like), and the precursors and protected forms of these groups. Additionally, a polar or polarizable group could be a macromonomer. More specific examples of such groups 30 follow.

Polar or polarizable groups may be derived from mono- or multifunctional carboxyl group containing molecules represented by the general formula:



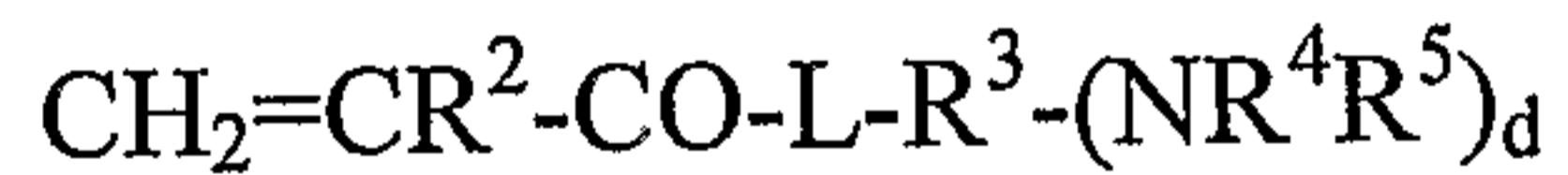
where  $\text{R}^2=\text{H}$ , methyl, ethyl, cyano, carboxy or carboxymethyl,  $d=1-5$  and G is a bond or a hydrocarbyl radical linking group containing from 1-12 carbon atoms of valence  $d+1$  and optionally substituted with and/or interrupted with a substituted or unsubstituted heteroatom (such as O, S, N and P). Optionally, this unit may be provided in its salt form. The preferred monomers in this class are acrylic acid, methacrylic acid, itaconic acid, and N-acryloyl glycine.

Polar or polarizable groups may, for example, be derived from mono- or multifunctional hydroxy group containing molecules represented by the general formula:



where  $\text{R}^2=\text{H}$ , methyl, ethyl, cyano, carboxy or carboxyalkyl,  $\text{L}=\text{O, NH}$ ,  $d=1-5$  and  $\text{R}^3$  is a hydrocarbyl radical of valence  $d+1$  containing from 1-12 carbon atoms. The preferred monomers in this class are hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, hydroxybutyl (meth)acrylate, glycerol mono(meth)acrylate, tris(hydroxymethyl)ethane monoacrylate, pentaerythritol mono(meth)acrylate, N-hydroxymethyl (meth)acrylamide, hydroxyethyl (meth)acrylamide, and hydroxypropyl (meth)acrylamide.

Polar or polarizable groups may alternatively be derived from mono- or multifunctional amino group containing molecules of the general formula:



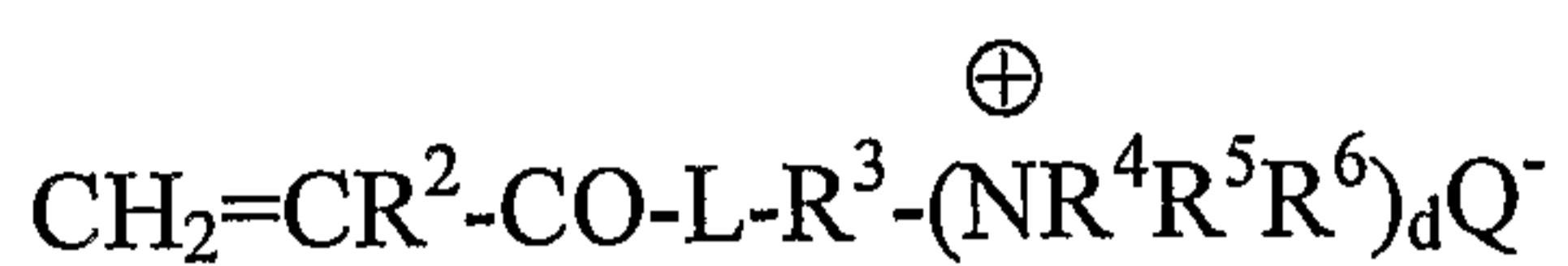
where  $\text{R}^2$ ,  $\text{L}$ ,  $\text{R}^3$ , and  $d$  are as defined above and  $\text{R}^4$  and  $\text{R}^5$  are H or alkyl groups of 1-12 carbon atoms or together they constitute a carbocyclic or heterocyclic group. Preferred monomers of this class are aminoethyl (meth)acrylate, aminopropyl (meth)acrylate, N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, N,N-dimethylaminopropyl (meth)acrylamide, N-isopropylaminopropyl (meth)acrylamide, and 4-methyl-1-acryloyl-piperazine.

Polar or polarizable groups may also be derived from alkoxy substituted (meth)acrylates or (meth)acrylamides such as methoxyethyl (meth)acrylate, 2-(2-

ethoxyethoxy)ethyl (meth)acrylate, polyethylene glycol mono(meth)acrylate or polypropylene glycol mono(meth)acrylate.

Polar or polarizable groups units may be derived from substituted or unsubstituted ammonium monomers of the general formula:

5



where  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{L}$  and  $d$  are as defined above, and where  $\text{R}^6$  is H or alkyl of 1-12 carbon atoms and  $\text{Q}^+$  is an organic or inorganic anion. Preferred examples of such 10 monomers include 2-N,N,N-trimethylammonium ethyl (meth)acrylate, 2-N,N,N-triethylammonium ethyl (meth)acrylate, 3-N,N,N-trimethylammonium propyl (meth)acrylate, N(2-N',N',N'-trimethylammonium) ethyl (meth)acrylamide, N-(dimethyl hydroxyethyl ammonium) propyl (meth)acrylamide, or combinations thereof, where the 15 counterion may include fluoride, chloride, bromide, acetate, propionate, laurate, palmitate, stearate, or combinations thereof. The monomer can also be N,N-dimethyl diallyl ammonium salt of an organic or inorganic counterion.

Ammonium group containing polymers can also be prepared by using as the polar or polarizable group any of the amino group containing monomer described above, and acidifying the resultant polymers with organic or inorganic acid to a pH where the pendant 20 amino groups are substantially protonated. Totally substituted ammonium group containing polymers may be prepared by alkylating the above described amino polymers with alkylating groups, the method being commonly known in the art as the Menschutkin reaction.

Polar or polarizable groups can also be derived from sulfonic acid group 25 containing monomers, such as vinyl sulfonic acid, styrene sulfonic acid, 2-acrylamido-2-methyl propane sulfonic acid, allyloxybenzene sulfonic acid, and the like. Alternatively, polar or polarizable groups may be derived from phosphorous acid or boron acid group-containing monomers. These monomers may be used in the protonated acid form as monomers and the corresponding polymers obtained may be neutralized with an organic 30 or inorganic base to give the salt form of the polymers.

Preferred repeating units of a polar or polarizable group include acrylic acid, itaconic acid, N-isopropylacrylamide, or combinations thereof.

In certain embodiments, the water-dispersible polymeric film formers disclosed herein also include a repeating unit that includes a fluoride releasing group. A preferred fluoride releasing group includes tetrafluoroborate anions as disclosed, for example, in U.S. Pat. No. 4,871,786 (Aasen et al.). A preferred repeating unit of a fluoride releasing group includes trimethylammoniummethyl methacrylate.

In certain embodiments, the water-dispersible polymeric film formers disclosed herein also include a repeating unit that includes a hydrophobic hydrocarbon group. An exemplary hydrophobic hydrocarbon group is derived from an ethylenically unsaturated preformed hydrocarbon moiety having a weight average molecular weight greater than 10 160. Preferably the hydrocarbon moiety has a molecular weight of at least 160. Preferably the hydrocarbon moiety has a molecular weight of at most 100,000, and more preferably at most 20,000. The hydrocarbon moiety may be aromatic or non-aromatic in nature, and optionally may contain partially or fully saturated rings. Preferred hydrophobic hydrocarbon moieties are dodecyl and octadecyl acrylates and methacrylates. Other 15 preferred hydrophobic hydrocarbon moieties include macromonomers of the desired molecular weights prepared from polymerizable hydrocarbons, such as ethylene, styrene, alpha-methyl styrene, vinyltoluene, and methyl methacrylate.

In certain embodiments, the water-dispersible polymeric film formers disclosed herein also include a repeating unit that includes a hydrophobic fluorine containing group. 20 Exemplary repeating units of hydrophobic fluorine-containing groups include acrylic or methacrylic acid esters of 1, 1-dihydroperfluoroalkanols and homologs:  $\text{CF}_3(\text{CF}_2)_x\text{CH}_2\text{OH}$  and  $\text{CF}_3(\text{CF}_2)_x(\text{CH}_2)_y\text{OH}$ , where x is zero to 20 and y is at least 1 up to 10;  $\omega$ -hydrofluoroalkanols ( $\text{HCF}_2(\text{CF}_2)_x(\text{CH}_2)_y\text{OH}$ ), where x is 0 to 20 and y is at least 1 up to 10; fluoroalkylsulfonamido alcohols; cyclic fluoroalkyl alcohols; and 25  $\text{CF}_3(\text{CF}_2\text{CF}_2\text{O})_q(\text{CF}_2\text{O})_x(\text{CH}_2)_y\text{OH}$ , where q is 2 to 20 and greater than x, x is 0 to 20, and y is at least 1 up to 10.

Preferred repeating units of a hydrophobic fluorine-containing group include 2-(methyl(nonafluorobutyl)sulfonyl)amino)ethyl acrylate, 2-(methyl(nonafluorobutyl)sulfonyl)amino)ethyl methacrylate, or combinations thereof.

In certain embodiments, the water-dispersible polymeric film formers disclosed herein also include a repeating unit that includes a graft polysiloxane chain. The graft polysiloxane chain is derived from an ethylenically unsaturated preformed organosiloxane

chain. The molecular weight of this unit is generally above 500. Preferred repeating units of a graft polysiloxane chain include a silicone macromer.

Monomers used to provide the graft polysiloxane chain of this invention are terminally functional polymers having a single functional group (vinyl, ethylenically 5 unsaturated, acryloyl, or methacryloyl group) and are sometimes termed macromonomers or "macromers". Such monomers are known and may be prepared by methods as disclosed, for example, in U.S. Pat. Nos. 3,786,116 (Milkovich et al.) and 3,842,059 (Milkovich et al.). The preparation of polydimethylsiloxane macromonomer and subsequent copolymerization with vinyl monomer have been described in several papers 10 by Y. Yamashita et al., [Polymer J. 14, 913 (1982); ACS Polymer Preprints 25 (1), 245 (1984); Makromol. Chem. 185, 9 (1984)].

In certain embodiments, the water-dispersible polymeric film formers disclosed herein also include a repeating unit that includes a modulating group. Exemplary 15 modulating groups are derived from acrylate or methacrylate or other vinyl polymerizable starting monomers and optionally contain functionalities that modulate properties such as glass transition temperature, solubility in the carrier medium, hydrophilic-hydrophobic balance and the like.

Examples of modulating groups include the lower to intermediate methacrylic acid esters of 1-12 carbon straight, branched or cyclic alcohols. Other examples of modulating 20 groups include styrene, vinyl esters, vinyl chloride, vinylidene chloride, acryloyl monomers and the like.

Preferred film formers are acrylate-based copolymers and urethane polymers such as the AVALURE series of compounds (e.g., AC-315 and UR-450), and carbomer-based 25 polymers such as the CARBOPOL series of polymers (e.g., 940NF), all available from Noveon, Inc., Cleveland, OH.

#### *OPTIONAL ADDITIVES*

Optionally, compositions of the present invention may contain solvents (e.g., 30 alcohols (e.g., propanol, ethanol), ketones (e.g., acetone, methyl ethyl ketone), esters (e.g., ethyl acetate), other nonaqueous solvents (e.g., dimethylformamide, dimethylacetamide, dimethylsulfoxide, 1-methyl-2-pyrrolidinone)), and water.

If desired, the compositions of the invention can contain additives such as indicators, dyes, pigments, inhibitors, accelerators, viscosity modifiers, wetting agents, tartaric acid, chelating agents, buffering agents, stabilizers, and other similar ingredients that will be apparent to those skilled in the art. Additionally, medicaments or other therapeutic substances can be optionally added to the dental compositions. Examples include, but are not limited to, fluoride sources, whitening agents, anticaries agents (e.g., xylitol), calcium sources, phosphorus sources, remineralizing agents (e.g., calcium phosphate compounds), enzymes, breath fresheners, anesthetics, clotting agents, acid neutralizers, chemotherapeutic agents, immune response modifiers, thixotropes, polyols, anti-inflammatory agents, antimicrobial agents, antifungal agents, agents for treating xerostomia, desensitizers, and the like, of the type often used in dental compositions. Combination of any of the above additives may also be employed. The selection and amount of any one such additive can be selected by one of skill in the art to accomplish the desired result without undue experimentation.

15

#### *METHODS OF USE*

Exemplary methods of using compositions of the present invention are described in the Examples. In some embodiments of the present invention, dental compositions of the present invention can be contacted with a tooth structure to treat the tooth structure. In some embodiments, placing a dental composition according to the present invention in an oral environment can effect remineralization, reduction of sensitivity, and/or protection of the tooth structure. In preferred embodiments, placing a dental composition according to the present invention in an oral environment delivers ions (e.g., calcium, phosphorus, and/or fluorine containing ions) to the oral environment.

Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. Unless otherwise indicated, all parts and percentages are on a weight basis, all water is deionized water, and all molecular weights are weight average molecular weight.

## EXAMPLES

### Test Methods

#### Compressive Strength (CS) Test Method

5 Compressive strength of a test sample was measured according to ANSI/ASA specification No. 27 (1993). A sample was packed into a 4-mm (inside diameter) glass tube; the tube was capped with silicone rubber plugs; and then the tube was compressed axially at approximately 0.28 MPa for 5 minutes. The sample was then light cured for 90 seconds by exposure to two oppositely disposed VISILUX Model 2500 blue light guns  
10 10 (3M Co., St. Paul, MN), followed by irradiation for 180 seconds in a Dentacolor XS unit (Kulzer, Inc., Germany). Cured samples were cut with a diamond saw to form 8-mm long cylindrical plugs for measurement of compressive strength. The plugs were stored in distilled water at 37°C for 24 hours prior to testing. Measurements were carried out on an Instron tester (Instron 4505, Instron Corp., Canton, MA) with a 10 kilonewton (kN) load  
15 cell at a crosshead speed of 1 mm/minute. Five cylinders of cured samples were prepared and measured with the results reported in MPa as the average of the five measurements.

#### Diametral Tensile Strength (DTS) Test Method

20 Diametral tensile strength of a test sample was measured according to ANSI/ASA specification No. 27 (1993). Samples were prepared as described for the CS Test Method, except that the cured samples were then cut into 2.2-mm thick disks for measurement of DTS. The disks were stored in water as described above and measured with an Instron tester (Instron 4505, Instron Corp.) with a 10 (kN) load cell at a crosshead speed of 1 mm/minute. Five disks of cured samples were prepared and measured with results reported  
25 in MPa as the average of the five measurements.

#### Work Time (WT) Test Method

30 The working time for a mixed cement to solidify was measured according to the following procedure. The tools and pastes were stored before use in a constant temperature and humidity room (22°C and 50% RH) and the procedure was conducted in the same room. Selected amounts of A and B pastes were mixed by a spatula on a pad for 25 seconds (sec) and the resulting mixed composition sample transferred into the semi-

cylindrical trough section (8-cm long, 1-cm wide and 3-mm deep) of an 8-cm by 10-cm plastic block. At time 1:00 min, perpendicular grooves were made using a ball point (1-mm diameter) groove maker across the trough every 30 sec; at 2:00 min, the grooves were made every 15 sec; and, closer to the end of the working time, the grooves were made 5 every 10 sec. The end of the working time was determined when the lumps of the cement sample moved with the groove maker. The working time was reported as the average of 2 or 3 measurements.

#### Visual Opacity (MacBeth Values) Test Method

10 Disc-shaped (1-mm thick x 15-mm diameter) paste samples were cured by exposing them to illumination from a VISILUX 2 curing light (3M Company, St. Paul, MN) for 60 seconds on each side of the disk at a distance of 6 mm. Hardened samples were measured for direct light transmission by measuring transmission of light through the thickness of the disk using a MacBeth transmission densitometer Model TD-903 equipped 15 with a visible light filter, available from MacBeth (MacBeth, Newburgh, NY). Lower MacBeth Values indicate lower visual opacity and greater translucency of a material. The reported values are the average of 3 measurements.

#### Spectral Opacity (SO) Test Method

20 ASTM-D2805-95 was modified to measure the spectral opacity for dental materials with thicknesses of approximately 1.0 mm. Disk-shaped, 1-mm thick by 20-mm diameter samples were cured by exposing them to illumination from a 3M Visilux-2 dental curing light for 60 seconds on each side of the disk at a distance of 6 mm. Y-tristimulus values for the disks were measured on an Ultrascan XE Colorimeter with a 3/8 inch 25 aperture (Hunter Associates Labs, Reston, VA) with separate white and black backgrounds. The D65 Illuminant was used with no filters for all measurements. A 10-degree angle of view was used. The Y-tristimulus values for the white and black substrates were 85.28 and 5.35, respectively. The spectral opacity is calculated as the ratio of the reflectance of a material on a black substrate to that of an identical material on a white 30 substrate. Reflectance is defined as equal to the Y-tristimulus value. Thus, spectral opacity =  $R_B/R_W$ , where  $R_B$  = reflectance of a disk on a black substrate and  $R_W$  = reflectance of the

same disk on a white substrate. Spectral opacity is unitless. Lower spectral opacity values indicate lower visual opacity and greater translucency of a material.

#### Adhesion to Dentin (AD) and Enamel (AE) Test Methods

5 Adhesion to dentin and adhesion to enamel were measured according to the procedure described in U.S. Pat. No. 6,613,812 (Bui et al.), except that a light cure exposure time of 20 seconds was used and 3M ESPE Filtek Z250 composite was used instead of 3M Z100 Restorative.

#### 10 X-Ray Diffraction (XRD) Test Method

A test sample was mulled in a boron carbide mortar and applied as an ethanol slurry to a zero background specimen holder (aluminum holder with quartz insert). Reflection geometry data were collected in the form of survey scans using a Philips vertical diffractometer, copper K $\alpha$  radiation, and proportional detector registry of the 15 scattered radiation. The crystallite sizes (D) for the crystalline phases present were calculated from observed peak widths after correction for instrumental broadening as the full width at half maximum using a Pearson VII peak shape model, accounting for  $\alpha_1/\alpha_2$  separation.

#### 20 Calcium and Phosphorus Ion Release (CIR) Test Method

Disk-shaped, 1-mm thick by 20-mm diameter samples were cured by exposing them to illumination from a 3M XL3000 dental curing light for 60 seconds on each side of the disk at a distance of 6 mm. The disks were stored in a HEPES-buffered solution at 37°C; the solution was exchanged periodically, and the ion content measured via 25 inductively coupled plasma spectroscopy (ICP) on a Perkin-Elmer 3300DV Optima ICP unit or via a calcium-selective electrode. The composition of the buffer solution was 1000 g deionized water, 3.38 g NaCl, and 15.61 g HEPES (N-2-hydroxyethylpiperazine-N'-2-ethanesulfonic acid). The ion release rate, microgram (ion)/g(disk)/day, was calculated by dividing the total ion content of the solution (concentration times volume of solution) by 30 the initial disk weight and by the time in days since the last exchange of buffer solution.

#### Dentin Remineralization Test Method

This method was carried out as described in "Surface Modulation of Dental Hard Tissues" (D. Tantbirojn, Ph.D. thesis, University of Minnesota, 1998), with the following exceptions. Dentin was used instead of enamel; the demineralizing solution was 0.1 ppm F<sup>-</sup> from NaF, 1.5 mM Ca<sup>+2</sup> from CaCl<sub>2</sub>, 0.9mM PO<sub>4</sub><sup>-3</sup> from KH<sub>2</sub>PO<sub>4</sub>, 50 mM acetic acid, 5 adjusted to pH=5.0 with 1M KOH; and the mineral content was measured by quantitative image analysis of microradiographs.

#### 10 Resistance to Demineralization in Dentin Test Method

This method was carried out as described in "Surface Modulation of Dental Hard Tissues" (D. Tantbirojn, Ph.D. thesis, University of Minnesota, 1998), with the following exceptions. Dentin was used instead of enamel; the demineralizing solution was 0.1 ppm F<sup>-</sup> from NaF, 1.5 mM Ca<sup>+2</sup> from CaCl<sub>2</sub>, 0.9mM PO<sub>4</sub><sup>-3</sup> from KH<sub>2</sub>PO<sub>4</sub>, 50 mM acetic acid, adjusted to pH=5.0 with 1M KOH; and the extent of acid erosion adjacent to 15 the sample was qualitatively categorized from microradiographs.

#### Abbreviations, Descriptions, and Sources of Materials

Abbreviation	Description and Source of Material
BisEMA6	Ethoxylated bisphenol A dimethacrylate (Sartomer, Exton, PA)
BisGMA	2,2-Bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane CAS No. 1565-94-2
TEGDMA	Triethyleneglycol dimethacrylate (Sigma-Aldrich, St. Louis, MO)
HEMA	2-Hydroxyethyl methacrylate (Sigma-Aldrich)
AA:ITA	Copolymer made from a 4:1 mole ratio of acrylic acid:itaconic acid, prepared according to Example 3 of U.S. Pat. No. 5,130,347 (Mitra), MW (average) = 106,000; polydispersity $\rho$ = 4.64.
IEM	2-Isocyanatoethyl methacrylate (Sigma-Aldrich)
VBP	Polymer made by reacting AA:ITA copolymer with

	sufficient IEM to convert 16 mole percent of the acid groups of the copolymer to pendent methacrylate groups, according to the dry polymer preparation of Example 11 of U.S. Pat. No. 5,130,347.
PM-2	KAYAMER PM-2; Bis(methacryloxyethyl) phosphate (Nippon Kiyaku, Japan)
MHP	Methacryloyloxyhexyl phosphate (See Preparation Method described herein)
CPQ	Camphorquinone (Sigma-Aldrich)
EDMAB	Ethyl 4-(N,N-dimethylamino)benzoate (Sigma-Aldrich)
DPIHFP	Diphenyl Iodonium Hexafluorophosphate (Johnson Matthey, Alpha Aesar Division, Ward Hill, NJ)
BHT	2,6-di-tert-butyl-4-methylphenol (Sigma-Aldrich)
Nalco 1042	Acidic colloidal silica sol (Nalco Corp., Naperville, IL)
Nalco 2329	Sodium hydroxide stabilized colloidal silica sol (Nalco Corp.)
A174	$\gamma$ -Methacryloxypropyltrimethoxysilane (OSI Specialties, Danbury CT)
Filler A	Nano-sized silica particles loosely aggregated as silica clusters were prepared in the form of a free-flowing dry powder according to the procedure for Example 1A (without separate calcining step) in U.S. Pat. Publication No. 2003/0181541 (Wu et al.), except that Nalco 1042 colloidal silica was used and the particles were not silane-treated.
Filler B	Nano-sized silica and zirconia particles loosely aggregated as substantially amorphous clusters were prepared in the form of a dry powder filler according to the procedure for “Cluster particles filler” in Column 22 of U.S. Pat. No. 6,572,693 (Wu et al.); except that the filler was not silane-treated and there was an additional firing step (550°C for 4 hours) after milling.
Filler C	Silane-treated fluoroaluminosilicate glass filler prepared as described for Filler B in U.S. Pat. Publication No. 2003/0198914

	(Brennan et al.)
Filler D	Nano-sized silica and zirconia particles loosely aggregated as substantially amorphous clusters were prepared in the form of a dry powder filler according to the procedure for "Cluster particles filler" in Column 22 of U.S. Pat. No. 6,572,693 (Wu et al.); except that the filler was not silane-treated.
PHOSCAL	Caseinate material comprising a casein phosphoprotein-calcium phosphate complex. (NSI Dental, Australia)
Vitrebond Powder	Powder component of VITREBOND Light Cure Glass Ionomer Liner/Base (3M Company, St. Paul, MN)
Vitrebond Liquid/Resin	Liquid component of VITREBOND Light Cure Glass Ionomer Liner/Base (3M Company)
Vitremer Liquid/Resin	Liquid component of VITREMER Restorative (3M Company)
AC-315	AVALURE acrylate-based polymer (Noveon, Inc., Cleveland, OH)

### Starting Materials Preparations

#### 6-Methacryloyloxyhexyl Phosphate (MHP)

5                   *6-Hydroxyhexyl Methacrylate* Synthesis: 1,6-Hexanediol (1000.00 g, 8.46 mol, Sigma-Aldrich) was placed in a 1-liter 3-neck flask equipped with a mechanical stirrer and a narrow tube blowing dry air into the flask. The solid diol was heated to 90°C, at which temperature all the solid melted. With continuous stirring, p-toluenesulfonic acid crystals (18.95 g, 0.11 mol) followed by BHT (2.42 g, 0.011 mol) and methacrylic acid (728.49.02 g, 8.46 mol). Heating at 90°C with stirring was continued for 5 hours during which time vacuum was applied using tap water aspirator for 5-10 minutes after each half-hour reaction time. The heat was turned off and the reaction mixture was cooled to room temperature. The viscous liquid obtained was washed with 10% aqueous sodium carbonate twice (2 x 240 ml), followed by washing with water (2 x 240 ml), and finally with 100 ml of saturated NaCl aqueous solution. The obtained oil was dried using anhydrous Na<sub>2</sub>SO<sub>4</sub> then isolated by vacuum filtration to give 1067 g (67.70 %) of 6-hydroxyhexyl

methacrylate, a yellow oil. This desired product was formed along with 15-18% of 1,6-bis(methacryloyloxyhexane). Chemical characterization was by NMR analysis.

6-Methacryloyloxyhexyl Phosphate (MHP) Synthesis: A slurry was formed by mixing P<sub>4</sub>O<sub>10</sub> (178.66 g, 0.63 mol) and methylene chloride (500 ml) in a 1-liter flask equipped with a mechanical stirrer under N<sub>2</sub> atmosphere. The flask was cooled in an ice bath (0-5°C) for 15 minutes. With continuous stirring, 6-hydroxyhexyl methacrylate (962.82 g, which contained 3.78 mol of the mono-methacrylate, along with its dimethacrylate by-product as described above) was added to the flask slowly over 2 hours. After complete addition, the mixture was stirred in the ice bath for 1 hour then at room temperature for 2 hours. BHT (500 mg) was added, and then the temperature was raised to reflux (40-41°C) for 45 minutes. The heat was turned off and the mixture was allowed to cool to room temperature. The solvent was removed under vacuum to afford 1085 g (95.5%) of 6-Methacryloyloxyhexyl Phosphate (MHP) as a yellow oil. Chemical characterization was by NMR analysis.

15

#### Resins A, B, C and D

Resins A, B, C and D were prepared by combining the ingredients as shown in Table 1.

Table 1. Compositions of Resins A, B, C, and D

Ingredient (Weight %)	Resin A	Resin B	Resin C	Resin D
VBP	43.43	43.00	0	0
HEMA	22.27	22.05	17.00	0
BisEMA6	0	0	0	32.00
BisGMA	0	0	27	0
TEGDMA	0	0	38	32.00
MHP	0	0	14.34	0
PM-2	0	0	0	33.15
Water	34.04	33.70	0	0
CPQ	0.30	0.30	0.32	0.3

DPIHFP	0	1.00	0.53	0
BHT	0.05	0.05	0.39	0.15
EDMAB	0	0	2.42	2.4
TOTAL:	100	100	100	100

### Examples 1A and 1B

#### Silica Nanocluster Filler Treated with Remineralization Agents

5       Example 1A. Filler A (nanocluster silica) (20 g) was mixed with deionized water (33.5 g) to afford a homogeneous, creamy slip. Separately, triethyl phosphate (2.24 g) was added to a 30% solution of calcium nitrate tetrahydrate in ethanol (4.82 g) and then mixed thoroughly with the Filler A slip. The theoretical final composition as oxides was calculated to be 10% by weight of CaO and P<sub>2</sub>O<sub>5</sub>, with Ca:P = 5:3. The resulting material 10 was gap-dried and then calcined as follows: 2hr ramp to 300°C/2hr, 2hr ramp to 550°C/4hr, 2hr to ambient. The resulting powder (designated Example 1A) was snowy white in color and X-Ray Diffraction (XRD) of the powder showed a substantial amorphous phase (a broad peak at d = 4.11 Å) with trace nanocrystalline peaks at d = 5.4 Å and d = 2.7 Å.

15       Example 1B. A 30% solution of calcium nitrate tetrahydrate in ethanol (4.80 g) was mixed with a 21% solution of P<sub>2</sub>O<sub>5</sub> in ethanol (4.19 g). To the resulting solution was added Filler A (22 g) and ethanol (8.58 g) in portions to form a homogeneous, pourable slip. (The theoretical final composition as oxides was calculated to be 10% by weight of CaO and P<sub>2</sub>O<sub>5</sub>, with Ca:P = 5:3.) The resulting material was dried in a glass tray at 80°C 20 overnight and then calcined as follows: 2hr ramp to 300°C/2hr, 2hr ramp to 550°C/4hr, 2hr to ambient. The resulting powder (designated Example 1B) was snowy white in color and XRD of the powder showed a broad peak at d = 4.07 Å (amorphous phase) with trace nanocrystalline peaks at d = 2.07 Å and d = 1.60 Å.

25       Example 1C. Triethyl phosphate (2.33 g) was added to a 30% solution of calcium nitrate tetrahydrate in ethanol (4.82 g) while stirring, after which ethanol (9.93 g) was added, followed by Filler A (nanocluster silica) (20 g), to afford a homogeneous, creamy slip. The resulting material was dried at 80°C, and then calcined as follows: 2hr ramp to 350°C/4hr, 2hr to ambient. The resulting powder (designated Example 1C) was snowy

white in color. The theoretical final composition as oxides was calculated to be 10% by weight of CaO and P<sub>2</sub>O<sub>5</sub>, with Ca:P = 5:3. Diffraction (XRD) of the powder showed only amorphous phase (a broad peak at d = 3.97 Å).

5

### Examples 1D – 1G

#### Silica Nanoparticle Filler Treated with Remineralization Agents

Example 1D. A 41 wt% solution of CaCl<sub>2</sub> in deionized water (100.5 g) was added to Nalco 1042 colloidal silica sol (52.5 g) while stirring. Then, a 44 wt% solution of K<sub>2</sub>HPO<sub>4</sub>·2H<sub>2</sub>O in deionized water (154 g) was added, after which the sol thickened 10 considerably. The sol was gap-dried, further dried in a glass tray at 125°C for 12 hours, and then crushed with a mortar and pestle. XRD of the resulting white powder (Example 1C) showed KCl nanocrystallites (D = >1500 Å) and CaPO<sub>3</sub>(OH) (monetite) (D = 1275 Å)

Example 1E. A 67 wt% solution of Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O in deionized water (76.1 g) was added to Nalco 1042 colloidal silica sol (221.5 g) while stirring. Then, a 50 wt% 15 solution of NH<sub>4</sub>PF<sub>6</sub> in deionized water (27.2 g) was added. The sol was gap-dried and then calcined as follows: 2hr ramp to 300°C/1hr, 2hr ramp to 550°C/4hr, 2hr to ambient. The powder was ball-milled for 8 hr. XRD of the resulting white powder (Example 1D) showed nanocrystalline CaF<sub>2</sub> (D = 255 Å), and nanocrystalline Ca(PO<sub>4</sub>)<sub>3</sub>(OH,F) (hydroxy- and/or fluoro-apatite) (D = 165 Å).

Example 1F. A 46 wt% solution of CaCl<sub>2</sub>·2H<sub>2</sub>O in deionized water (64.4 g) was 20 added to Nalco 2329 colloidal silica sol (429.3 g) while stirring. Then, a 16 wt% solution of Na<sub>2</sub>FPO<sub>3</sub> in deionized water (188.8 g) was added to yield a thin, pale white sol. The sol was gap-dried. XRD of the resulting white powder (Example 1E) showed a broad peak at d = 3.86 Å (amorphous phase) and NaCl nanocrystallites (D ≥ 1500 Å).

Example 1G. A 46 wt% solution of CaCl<sub>2</sub>·2H<sub>2</sub>O in deionized water (64.5 g) was 25 added to Nalco 1042 colloidal silica sol (355.8 g) while stirring. Then, a 16 wt% solution of Na<sub>2</sub>FPO<sub>3</sub> in deionized water (189 g) was added to yield a thin, slightly turbid sol. The sol was gap-dried. XRD of the resulting white powder (Example 1F) showed a broad peak at d = 3.96 Å (amorphous phase) and NaCl nanocrystallites (D ≥ 1500 Å).

30

### Examples 2A – 2Q

## Zirconia-Silica Nanocluster Filler Treated with Remineralization Agents

Example 2A. Filler B (nanocluster zirconia-silica) (100 g) was mixed with deionized water (70.2 g) to afford a homogeneous, creamy slip. Separately, a 67% solution of calcium nitrate tetrahydrate in deionized water (2.29 g) was mixed with a 50% solution of  $\text{NH}_4\text{PF}_6$  in deionized water (4.01 g) and then mixed into the Filler B slip. The theoretical final composition was calculated to be 2% by weight of  $\text{Ca}(\text{PF}_6)_n$  with  $\text{Ca:PF}_6 = 1:2$ . The resulting material was gap-dried and then calcined as follows: 2hr ramp to 300°C/2h, 2hr ramp to 550°C/4hr, 2hr to ambient. The resulting powder (designated Example 2A) was snowy white in color and XRD of the powder showed a broad peak at  $d = 3.86 \text{ \AA}$  due to the amorphous portion, and monoclinic zirconia nanocrystals with crystallite size  $D = 65 \text{ \AA}$ .

Example 2B. Filler B (nanocluster zirconia-silica) (50.3 g) was mixed with deionized water (42 g) to afford a homogeneous, smooth slip. Separately, a 30% solution of calcium nitrate tetrahydrate in ethanol (3.26 g) was mixed with triethyl phosphate (3.87 g) and then mixed into the Filler B slip. The slip thickened noticeably on adding the calcium-phosphate blend. (The theoretical final composition as oxides was calculated to be 4% by weight of  $\text{CaO}$  and  $\text{P}_2\text{O}_5$ , with  $\text{Ca:P} = 5:3$ .) The resulting material was gap-dried and then calcined as follows: 2hr ramp to 300°C/2hr, 2hr ramp to 550°C/4hr, 2hr to ambient. The resulting powder (designated Example 2B) was snowy white in color and XRD of the powder showed a broad peak at  $d = 3.92 \text{ \AA}$  (amorphous phase), and monoclinic zirconia nanocrystals with crystallite size  $D = 55 \text{ \AA}$ .

Example 2C. A sodium phosphate solution was prepared by mixing deionized water (290.1 g) with  $\text{Na}_2\text{HPO}_4$  (47.5 g),  $\text{Na}_4\text{P}_2\text{O}_7$  (3.1 g), and 1M  $\text{NaOH}$  (335 g). Separately, Filler B (nanocluster zirconia-silica) (80 g) was mixed with deionized water (22.7 g) and a 67% solution of calcium nitrate tetrahydrate in deionized water (53.3 g). The resulting slip was added to the sodium phosphate solution (67.6 g) to form a thin, dilatent slip that was put under vacuum for 10 minutes and then dried in an oven at 60°C for 3 hours. XRD of the resulting powder (designated Example 2C) showed a broad peak at  $d = 3.87 \text{ \AA}$  (amorphous phase), and monoclinic zirconia nanocrystals with crystallite size  $D = 65 \text{ \AA}$ .

Examples 2D and 2E. Filler B (nanocluster zirconia-silica) (200 g) was mixed with deionized water (206 g) and  $\text{Na}_2\text{FPO}_3$  (10.44 g) under vigorous stirring to form a thin

slurry. A 67% solution of calcium nitrate tetrahydrate in deionized water (23.1 g) was then added to the slurry that thickened noticeably. (The theoretical final composition was calculated to be 5% by weight of  $\text{Ca}(\text{FPO}_3)_n$  with  $\text{Ca}:\text{FPO}_3 = 1:1$ .) The resulting material was gap-dried to yield a fine, white powder. XRD of the powder (designated Example 2D) 5 showed a broad peak at  $d = 3.93 \text{ \AA}$  (amorphous phase), and monoclinic zirconia nanocrystals with crystallite size  $D = 45 \text{ \AA}$ , and  $\text{NaCl}$  nanocrystallites ( $D = 45 \text{ \AA}$ ). A sample of the powder was further heated at  $150^\circ\text{C}$  for 6 hours to provide a new powder (designated Example 2E), for which XRD showed a broad peak at  $d = 3.86 \text{ \AA}$  (amorphous phase),  $\text{NaCl}$  nanocrystallites basically unchanged, and monoclinic zirconia nanocrystals 10 with crystallite size decreased slightly to  $D = 30 \text{ \AA}$ .

Example 2F. Filler B (nanocluster zirconia-silica) (200 g) was mixed with deionized water (130.4 g) and a 46% solution of calcium chloride dihydrate in deionized water (69.1 g) under vigorous stirring to form a slurry. A 50% solution of  $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$  in deionized water (110.9 g) was then added to the slurry. (The theoretical final 15 composition as oxides was calculated to be 6.1% by weight of  $\text{CaO}$  and 3.9% by weight  $\text{P}_2\text{O}_5$  with  $\text{Ca:P} = 2:1$ .) The resulting material was gap-dried to yield a fine, white powder that was further heated at  $125^\circ\text{C}$  for 12 hours. XRD of the resulting powder (designated Example 2F) showed a broad peak at  $d = 3.95 \text{ \AA}$  (amorphous phase), monoclinic zirconia nanocrystals with crystallite size  $D = 70 \text{ \AA}$ , and  $\text{NaCl}$  nanocrystallites ( $D \geq 1500 \text{ \AA}$ ).

Example 2G. Filler B (nanocluster zirconia-silica) (200.5 g) was mixed with deionized water (152.7 g) and a 67% solution of calcium nitrate tetrahydrate in deionized water (55.8 g) under vigorous stirring to form a slurry. A 50% solution of  $\text{NH}_4\text{H}_2\text{PO}_4$  in deionized water (147.3 g) was then added to the slurry. An amount of poly( $\text{N}$ -vinylpyrrolidone) was mixed into the slurry equaling 6% of the weight of the slurry. The 20 theoretical final composition as oxides was calculated to be 4.4% by weight of  $\text{CaO}$  and 5.6% by weight  $\text{P}_2\text{O}_5$  with  $\text{Ca:P} = 1:1$ . The resulting material was gap-dried to yield soft flakes that were calcined as follows:  $3^\circ\text{C}/\text{min}$  ramp to  $300^\circ\text{C}/2\text{hr}$ ,  $2^\circ\text{C}/\text{min}$  ramp to 25  $550^\circ\text{C}/6\text{hr}$ ,  $5^\circ\text{C}/\text{hr}$  to ambient. XRD of the resulting powder (designated Example 2G) showed a broad peak at  $d = 3.81 \text{ \AA}$  (amorphous phase),  $\text{Ca}_3(\text{PO}_4)_2$  ( $D = 340 \text{ \AA}$ ), monoclinic zirconia nanocrystals with crystallite size  $D = 70 \text{ \AA}$ , and  $\text{NaCl}$  nanocrystallites ( $D \geq 1500 \text{ \AA}$ ). 30

Example 2H. A 30% solution of calcium nitrate tetrahydrate in ethanol (109.7 g) was mixed with ethanol (48 g) and Filler B (nanocluster zirconia-silica) (180 g) to form a homogeneous, smooth slip. Triethyl phosphate (25.8 g) was then added. (The theoretical final composition as oxides was calculated to be 10% by weight of CaO and P<sub>2</sub>O<sub>5</sub> with Ca:P = 1:1.) The resulting material was gap-dried and then calcined as follows: 3hr ramp to 400°C/4hr, 2hr to ambient. XRD of the resulting snowy white powder (designated Example 2H) showed a broad peak at d = 3.92 Å (amorphous phase), and monoclinic zirconia nanocrystals with crystallite size D = 55 Å.

Example 2I. Filler B (nanocluster zirconia-silica) (45.1 g) was mixed with deionized water (59.4 g) and PHOSCAL (5.2 g) to form a thin, smooth, homogeneous slurry. The slurry was gap-dried on the same day to yield thin, friable flakes that crushed readily to a powder. The final powder (designated Example 2I) contained 10% PHOSCAL and 90% Filler B.

Examples 2J and 2K. Filler B (nanocluster zirconia-silica) (200 g) was mixed with ethanol (105 g) and a 30% solution of calcium nitrate tetrahydrate in ethanol (167.1 g). A solution of 21% P<sub>2</sub>O<sub>5</sub> in ethanol (14.6 g) was then added to yield a thin, homogeneous slurry that was gap-dried on the same day to yield soft granules that crushed readily to a powder (designated Example 2J). (The theoretical final composition as oxides was calculated to be 10% by weight of CaO and P<sub>2</sub>O<sub>5</sub> with Ca:P = 5:1.) A sample of the powder was heated at 150°C for 16 hours to provide a new powder (designated Example 2K). XRD of the two powders were substantially identical in crystal structure with a broad peak at d = 3.8-4.0 Å (amorphous phase) and monoclinic zirconia nanocrystals with crystallite size D = 35-40 Å.

Example 2L and 2M. Filler B (nanocluster zirconia-silica) (150.8 g) was mixed with ethanol (14 g) and a 30% solution of calcium nitrate tetrahydrate in ethanol (133.8 g). A solution of 21% P<sub>2</sub>O<sub>5</sub> in ethanol (34.6 g) was then added to yield a homogeneous slurry that was gap-dried 5 days later to yield a powder (designated Example 2L). (The theoretical final composition as oxides was calculated to be 10% by weight of CaO and P<sub>2</sub>O<sub>5</sub> with Ca:P = 5:3.) A sample of the powder was heated at 150°C for 16 hours to provide a new powder (designated Example 2M). XRD of the powder showed a broad peak at d = 3.85 Å (amorphous phase) and monoclinic zirconia nanocrystals with crystallite size D = 40 Å.

Example 2N. A 67% solution of calcium nitrate tetrahydrate in deionized water (11.1 g) was mixed with deionized water (191 g) followed by the addition of a 50% solution of  $\text{NH}_4\text{PF}_6$  in deionized water (19.8 g) to form a clear solution. Filler B (nanocluster zirconia-silica) (200 g) was then added to yield a smooth, homogeneous, 5 pourable slurry that was gap-dried on the same day. (The theoretical final composition was calculated to be 5% by weight of  $\text{Ca}(\text{PF}_6)_n$  with  $\text{Ca:PF}_6 = 1:2$ .) The resulting powder was calcined as follows: 3hr to 400°C/6hr, 2hr to ambient to yield a snowy white, friable powder (designated Example 2N). XRD of the powder showed a broad peak at  $d = 3.94 \text{ \AA}$  (amorphous phase) and monoclinic zirconia nanocrystals with crystallite size  $D = 50 \text{ \AA}$ .

10 Example 2O. A 67% solution of calcium nitrate tetrahydrate in deionized water (21.6 g) was mixed with deionized water (158.5 g) followed by the addition of a 50% solution of  $\text{NH}_4\text{PF}_6$  in deionized water (39.7 g) to form a clear solution. Filler B (nanocluster zirconia-silica) (200 g) was then added to yield a smooth, homogeneous, pourable slurry that was gap-dried on the same day. (The theoretical final composition was 15 calculated to be 10% by weight of  $\text{Ca}(\text{PF}_6)_n$  with  $\text{Ca:PF}_6 = 1:2$ .) The resulting powder was calcined at 3hr to 400°C/6hr, 2hr to ambient to yield a snowy white, friable powder (designated Example 2O). XRD of the powder showed a broad peak at  $d = 3.97 \text{ \AA}$  (amorphous phase) and monoclinic zirconia nanocrystals with crystallite size  $D = 55 \text{ \AA}$ .

15 Example 2P. A 67% solution of calcium nitrate tetrahydrate in deionized water (10.8 g) was mixed with deionized water (180 g) and Filler D (270 g) to form a homogeneous, creamy slip. A 50% solution of  $\text{NH}_4\text{PF}_6$  in deionized water (20 g) was then added under vigorous stirring to yield a slip that was gap-dried to afford a snowy white powder (designated Example 2P). The theoretical final composition was calculated to be 5% by weight of  $\text{Ca}(\text{PF}_6)_n$  with  $\text{Ca:PF}_6 = 1:2$ .

20 Example 2Q. Filler B (nanocluster zirconia-silica) (60.5 g) was slurried in deionized water (125.5 g), to which was then added a 10% solution of trifluoroacetic acid in deionized water (1.43 g) followed by A-174 (4.50 g) The resulting thin slurry was allowed to react for 2 hr under vigorous stirring. Then, a 46 wt% solution of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  in deionized water (14.1 g) was added, followed by a 16 wt% solution of  $\text{Na}_2\text{FPO}_3$  in 25 deionized water (10.44 g). The resulting slurry was dried in a glass tray at 80°C for 9 hr.

#### Examples 2AA – 2JJ

Hardenable Resins Containing Fillers Treated with Remineralization Agents

Example 2AA. Example 2G filler (55%) was added to Resin C to yield a paste that was designated Example 2AA.

5       Example 2BB. Example 2A filler (55%) was added to Resin C to yield a paste that was designated Example 2BB.

Example 2CC. Example 1G filler (55%) was added to Vitremer Resin to yield a paste that was designated Example 2CC.

Example 2DD. Example 1F filler (55%) was added to Resin C to yield a paste that was designated Example 2DD.

10       Example 2EE. Example 1D filler (55%) was added to Vitremer Resin to yield a paste that was designated Example 2EE.

Example 2FF. Example 1D filler (55%) was added to Resin C to yield a paste that was designated Example 2FF.

15       Example 2GG. Example 1E filler (55%) was added to Vitremer Resin to yield a paste that was designated Example 2GG.

Example 2HH. Example 1E filler (55%) was added to Resin C to yield a paste that was designated Example 2HH.

Example 2II. Example 1F filler (55%) was added to Vitremer Resin to yield a paste that was designated Example 2II.

20       Example 2JJ. A portion (3.5 g) of Example 2Q filler was mixed with Resin D (2.4 g) to yield a thin, flowable paste (Example 2JJ). A light-cured, 1-mm thick disk of the paste had a Visual Opacity of 0.347 measured on a Macbeth densitometer.

Example 2KK. Example 1G filler (55%) was added to Vitremer Resin to yield a paste that was designated Example 2KK.

25       Example 2LL. Example 1F filler (55%) was added to Resin C to yield a paste that was designated Example 2LL.

Examples 3-8 and Comparative Examples 1-2

30       RMGI Compositions Containing  
Nanocluster Fillers Treated with Remineralization Agents

Nanofiller cluster fillers treated with remineralizing agents (Powder 2 - Examples 1A, 1C, 2J, 2A, and 2I) were mixed with Vitrebond Powder (Powder 1) and then with various liquid resins to afford homogeneous RMGI pastes designated Examples 3-8, respectively. These pastes were evaluated for compressive strength (CS), diametral tensile strength (DTS), work time, spectral opacity, and adhesion to dentin (AD) and enamel (AE) according to the Test Methods described herein and the results compared to those from the commercial VITREBOND (VB) Light Cure Glass Ionomer Liner/Base product (Comparative Examples (CE) 1 and 2). (For the AD and AE tests of these materials, an additional step was added: a dental adhesive (3M ESPE Singlebond Plus dental adhesive) was brushed over the cured material and then light-cured for 10 sec before application of the composite.) The paste compositions are provided in Table 2A and the evaluation results in Table 2B.

Table 2A

Example	Powder 1	Powder 2	Liquid Resin	P1/P2/L
3	Vitrebond	Example 1A	Vitremer	0.5/0.5/1
4	Vitrebond	Example 1C	Resin B	1.08/0.12/1
5	Vitrebond	Example 1C	Resin B	1.14/0.06/1
6	Vitrebond	Example 2J	Resin B	1.14/0.06/1
7	Vitrebond	Example 2A	Vitremer	0.5/0.5/1
8	Vitrebond	Example 2I	Resin B	0.5/0.5/1
CE 1	Vitrebond	None	Vitrebond	1.4/0/1
CE 2	Vitrebond	None	Vitrebond	1.2/0/1

Table 2B

Example	Spectral Opacity	CS MPa (SD)	DTS MPa (SD)	Work Time Min:Sec	Dentin Adhesion MPa (SD)	Enamel Adhesion MPa (SD)
3	65.7	40 (1.84)	7.38 (0.60)	4:55	0.00 (0.00)	NT
4	NT*	92 (6.53)	19.39 (1.60)	NT	10.18 (3.22)	8.77 (2.03)
5	NT	117 (5.19)	20.42 (1.93)	5:05	9.05 (0.99)	8.94 (4.12)
6	NT	92 (10.42)	15.46 (1.12)	NT	5.85 (1.88)	12.01 (1.55)
7	68.4	104 (5.11)	18.63 (1.87)	NT	5.22 (1.66)	9.19 (2.99)
8	74.2	86 (7.38)	15.80 (1.63)	NT	6.90 (1.56)	NT
CE 1	77.2	113 (9.50)	25.32 (1.73)	4:45	6.86 (5.59)	12.94 (1.03)
CE 2	NT	108 (6.55)	21.60 (0.89)	NT	NT	NT

5

\*NT – Not Tested

## Examples 9-14

## Acidic Resin Compositions Containing

## Nanocluster Fillers Treated with Remineralization Agents

Acidic resin compositions containing nanocluster fillers treated with

5 remineralization agents (Examples 9-14) were prepared by combining the ingredients shown in Table 3. The resulting paste compositions were evaluated for compressive strength (CS), diametral tensile strength (DTS), spectral opacity, and adhesion to dentin and enamel according to the Test Methods described herein and the results are provided in Table 3. (For the AD and AE tests of these materials, a thin layer of the material was applied and allowed to sit for 30 sec before light-curing for 30 sec.) The compositions 10 showed excellent strength and adhesion to tooth structure.

Table 3

Example	Composition (Numbers are Weight %)	Spectral Opacity	CS MPa (SD)	DTS MPa (SD)	Dentin Adhesion MPa (SD)	Enamel Adhesion MPa (SD)
9	Example 2D - 55 Resin C - 45	28.9	244 (41)	45 (5.3)	5.23 (0.94)	23.60 (8.20)
10	Example 2H - 55 Resin C - 45	40.3	263 (50)	35 (19.9)	1.42 (1.99)	25.30 (12.86)
11	Example 2F - 55 Resin C - 45	49.9	162 (31)	24 (3.1)	8.45 (1.18)	8.11 (2.95)
12	Example 2J - 55 Resin C - 45	29.7	93 (26)	11 (0.3)	3.52 (1.25)	6.40 (1.35)
13	Example 2I - 40 Resin D - 45 Filler C - 15	45.7	180 (52)	28 (8.7)	NT	NT
14	Example 2D - 55 Resin D - 45	35.8	237 (30)	35 (3.6)	7.29 (1.16)	1.37 (0.66)

## Example 15

Tooth Coating Compositions Containing  
Nanocluster Filler Treated with Remineralization Agents

Example 2P (1.6 g) was blended with a solution of 25% AVALURE AC-315 polymer in ethanol (1.5 g) to form a turbid dispersion that was designated Example 15.

5 The dispersion formed a hard, cloudy coating (i.e., film) after applying onto a glass slide and drying. A glass slide partially coated with this dispersion and dried was held in deionized water for 62 hours under ambient conditions. The film remained visually intact and displayed no weight loss.

10

Calcium Ion Release Evaluations

Filler Examples 1A, 1B, 2A, 2B, 2C, 2D, 2F, 2G, 2H, 2N; RMGI Examples 3, 7, and 8; Filler plus Acid Resin Examples 9 and 10; and Filler plus Hardenable Resin Examples 2AA-2II were evaluated for calcium and phosphorus release over time according to the Test Method described herein. Results are reported for the ICP method (calcium and phosphorus ions via inductively coupled plasma spectroscopy) and for the calcium-selective electrode (Ca-E) method (calcium ions only) and are provided in Table 15 4.

20

25

Table 4  
 Release of Calcium and Phosphorus Ions over Time  
 All Values in Units of Microgram (Ion)/g (Disk)/day

Ex.	Day 7				Day 30				Day 60				Day 180				
	ICP Ca	ICP P	Ca-E Ca	Ca-E P	ICP Ca	ICP Ca-E	ICP Ca	ICP P	Ca-E Ca	Ca-E Ca	ICP Ca	ICP P	Ca-E Ca	Ca-E Ca	ICP Ca	ICP P	
2C	385.9	630.6	NT	72.21	41.95	NT	41.05	8.88	NT	NT	NT	NT	NT	NT	NT	NT	8.83
2G	202.0	362.2	NT	43.79	48.80	NT	24.94	30.00	NT	NT	NT	NT	NT	NT	NT	NT	7.52
2F	NT	411.4	NT	91.26	27.02	NT	44.73	11.47	NT	NT	NT	NT	NT	NT	NT	NT	9.70
2B	71.42	127.4	NT	15.46	31.00	NT	9.48	15.50	NT	NT	NT	NT	NT	NT	NT	NT	1.35
1B	336.0	971.2	NT	38.42	35.13	NT	23.76	8.63	NT	NT	NT	NT	NT	NT	NT	NT	3.97
1A	299.1	650.7	NT	53.95	33.00	NT	25.30	5.36	NT	NT	NT	NT	NT	NT	NT	NT	3.40
2H	545.5	94.14	NT	81.02	12.05	NT	48.31	4.60	NT	NT	NT	NT	NT	NT	NT	NT	9.52
2A	28.2	49.30	NT	8.15	27.81	NT	6.31	6.25	NT	NT	NT	NT	NT	NT	NT	NT	1.33
2N	117.1	150.8	NT	20.35	27.40	NT	11.14	12.31	NT	NT	NT	NT	NT	NT	NT	NT	2.73
2D	493.0	449.8	NT	49.83	27.47	NT	NT	28.09	NT	NT	NT	NT	NT	NT	NT	NT	3.19

TABLE 4 (continued)

3	NT	NT	4.34	NT	8.55	NT	NT	5.77	NT	NT	NT
7	NT	NT	4.07	NT	4.52	NT	NT	3.22	NT	NT	NT
8	NT	NT	1.87	NT	2.72	NT	NT	3.92	NT	NT	3.17
9	NT	NT	58.93	NT	7.52	NT	NT	6.56	NT	NT	4.20
10	NT	NT	50.96	NT	38.81	NT	NT	22.17	NT	NT	15.20
2AA	46.71	60.22	NT	16.88	19.86	NT	5.86	11.87	NT	NT	1.75
2BB	18.73	91.45	NT	6.45	8.03	NT	6.16	3.68	NT	NT	NT
2CC	2053	2852	NT	352.7	523.8	NT	240.5	268.5	NT	NT	71.87
2DD	713.1	768.7	NT	338.9	309.6	NT	165.4	125.2	NT	NT	NT
2EE	132.5	295.1	NT	63.43	55.63	NT	59.47	32.72	NT	NT	17.18
2FF	111.7	281.2	NT	19.41	50.55	NT	16.11	14.90	NT	NT	NT
2GG	1552	2641	NT	145.7	93.96	NT	NT	73.65	NT	NT	12.85
2HH	NT	NT	192.2	NT	41.43	NT	NT	32.70	NT	NT	20.70
2II	2276	2541	NT	178.6	91.74	NT	NT	76.27	NT	NT	11.49

### Dentin Remineralization Evaluations

Example 3 (RMGI composition in which the powder component includes 5 nanocluster silica treated with calcium and phosphate agents) was evaluated for dentin remineralization according to the Test Method described herein and showed good remineralization after 3 weeks adjacent to the applied cement in the area of the exposed lesion.

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### Resistance to Demineralization in Dentin Evaluations

RMGI Examples 6, 7, and 8; and comparative Examples 1 and 5 (VITREBOND Light Cure Glass Ionomer Liner/Base and FILTEK Z250 Universal Restorative System) were evaluated for resistance to demineralization in dentin according to the Test Method described herein. The resulting 15 microradiographs and associated data (Table 5) showed that all of the FILTEK Z250 samples had full lesions, as expected for a material with no fluoride release or remineralization potential. The VITREBOND product enhanced resistance to acid attack versus FILTEK Z250 and Examples 6-8 all enhanced the resistance even more, with fewer samples at “full lesion” and more with mineral present 20 near the applied cements.

Table 5

Percent of Samples in Each Lesion Category

Lesion Category	VITREBOND	Z250	Ex. 6	Ex. 7	Ex. 8
Full Lesion	27.3	100.0	18.2	9.5	10.5
Lesion thinner near material	33.3	0.0	13.6	47.6	31.6
Intact dentin near material, lesion farther away	39.4	0.0	68.2	42.9	57.9
No lesion discernible	0.0	0.0	0.0	0.0	0.0

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. It should be understood that this invention is not intended to be unduly limited by the illustrative embodiments and examples set forth herein and 5 that such examples and embodiments are presented by way of example only with the scope of the invention intended to be limited only by the claims set forth herein as follows.

10

What is claimed is:

1. A dental filler comprising a treated surface, wherein the treated surface comprises phosphorus and a divalent cation selected from the group consisting of Mg, Ca, Sr, Ba, Zn, and combinations thereof.
2. The dental filler of claim 1, wherein the treated surface comprises a source of divalent cations selected from the group consisting of Mg, Ca, Sr, Ba, Zn, and combinations thereof.
3. The dental filler of claim 1, wherein the treated surface comprises a source of phosphate ions.
4. The dental filler of claim 1 wherein the treated surface is amorphous.
5. The dental filler of claim 1 wherein the treated surface is at least partially crystalline.
6. The dental filler of claim 1, wherein the dental filler is porous.
7. The dental filler of claim 6, wherein the porous dental filler is selected from the group consisting of porous particles, porous agglomerates of particles, and combinations thereof.
8. The dental filler of claim 1, wherein the dental filler comprises nanoparticles, agglomerates of nanoparticles, or combinations thereof.
9. The dental filler of claim 1, wherein the dental filler comprises metal oxides, metal fluorides, metal oxyfluorides, or combinations thereof.
10. The dental filler of claim 9, wherein the metal is selected from the group consisting of heavy metals, non-heavy metals, and combinations thereof.

11. The dental filler of claim 1, wherein the dental filler is an oxide, a fluoride, or an oxyfluoride of an element selected from the group consisting of Groups 2-5 elements, Groups 12-15 elements, Lanthanide elements, and combinations thereof.
12. The dental filler of claim 11, wherein the element is selected from the group consisting of Ca, Sr, Ba, Y, La, Ce, Pr, Nd, Pm, Sm Eu, Gd, Tb, Dy, Ho, Er, Tm Yb, Lu, Ti, Zr, Ta, Zn B, Al, Si, Sn, P, and combinations thereof.
13. The dental filler of claim 1, wherein the dental filler comprises a glass, an amorphous material, or a crystalline material.
14. The dental filler of claim 1, wherein the dental filler comprises a source of fluoride ions.
15. The dental filler of claim 14, wherein the dental filler comprises a fluoroaluminosilicate glass.
16. The dental filler of claim 1, wherein the treated surface comprises calcium phosphate.
17. The dental filler of claim 1, wherein the treated surface further comprises a silane.
18. The dental filler of claim 1, wherein the treated surface further comprises a source of fluoride ions.
19. The dental filler of claim 1, wherein the treated surface further comprises a source of aluminum ions.

20. The dental filler of claim 1, wherein the treated surface further comprises an antibacterial agent.
21. A method of making a dental filler comprising a treated surface, the method comprising treating the surface of the dental filler with a phosphorus precursor and a precursor for a divalent cation selected from the group consisting of Mg, Ca, Sr, Ba, Zn, and combinations thereof.
22. The method of claim 21, wherein treating is selected from the group consisting of coating, infiltrating, and combinations thereof.
23. The method of claim 21, wherein treating comprises:  
dissolving, dispersing, or suspending the phosphorus precursor and the precursor for the divalent cation in one or more liquids;  
combining the one or more liquids with the dental filler; and  
removing at least a portion of the one or more liquids to provide the treated surface.
24. The method of claim 23 wherein the liquid is non-aqueous.
25. The method of claim 23 wherein the liquid comprises water.
26. The method of claim 23 further comprising heating the dental filler.
27. The method of claim 21, wherein the phosphorus precursor is selected from the group consisting phosphoric acid and salts thereof, pyrophosphoric acid and salts thereof, monofluorophosphoric acid and salts thereof, hexafluorophosphoric acid and salts thereof, phosphate esters, glycerophosphates, caseinates, phosphorous oxides, phosphorus oxyhalides, and combinations thereof.

28. The method of claim 21, wherein the precursor for the divalent cation comprises an organic or inorganic salt of the cation, a basic or oxy salt thereof, or combinations thereof.
29. The method of claim 28 wherein the precursor for the divalent cation comprises an anion selected from the group consisting of nitrate, halide, hydroxide, alkoxide, caseinate, carboxylate, and combinations thereof.
30. The method of claim 23, wherein removing at least a portion of the one or more liquids comprises spray drying, oven drying, gap drying, lyophilizing, or combinations thereof.
31. The method of claim 21, wherein the treated surface comprises a source of divalent cations selected from the group consisting of Mg, Ca, Sr, Ba, Zn, and combinations thereof.
32. The method of claim 21, wherein the treated surface comprises a source of phosphate ions.
33. The method of claim 21, wherein the dental filler is porous.
34. The method of claim 33, wherein the porous dental filler is selected from the group consisting of porous particles, porous agglomerates of particles, and combinations thereof.
35. The method of claim 21, wherein the dental filler comprises nanoparticles, agglomerates of nanoparticles, or combinations thereof.
36. The method of claim 21, wherein the dental filler comprises metal oxides, metal fluorides, metal oxyfluorides, or combinations thereof.

37. The method of claim 36, wherein the metal is selected from the group consisting of heavy metals, non-heavy metals, and combinations thereof.
38. The method of claim 21, wherein the dental filler is an oxide, a fluoride, or an oxyfluoride of an element selected from the group consisting of Groups 2-5 elements, Groups 12-15 elements, Lanthanide elements, and combinations thereof.
39. The method of claim 38, wherein the element is selected from the group consisting of Ca, Sr, Ba, Y, La, Ce, Pr, Nd, Pm, Sm Eu, Gd, Tb, Dy, Ho, Er, Tm Yb, Lu, Ti, Zr, Ta, Zn B, Al, Si, Sn, P, and combinations thereof.
40. The method of claim 21, wherein the dental filler comprises a glass, an amorphous material, or a crystalline material.
41. The method of claim 21, wherein the dental filler comprises a source of fluoride ions.
42. The method of claim 41, wherein the dental filler comprises a fluoroaluminosilicate glass.
43. The method of claim 21, wherein the treated surface comprises calcium phosphate.
44. The method of claim 21, wherein the treated surface further comprises a silane.
45. The method of claim 21, wherein the treated surface further comprises a source of fluoride ions.
46. The method of claim 21, wherein the treated surface further comprises a source of aluminum ions.

47. The method of claim 21, wherein the treated surface further comprises an antibacterial agent.
48. A dental composition comprising a dental filler according to claim 1.
49. The dental composition of claim 48 further comprising an additional filler.
50. The dental composition of claim 48 further comprising water.
51. The dental composition of claim 48 further comprising a water-dispersible, polymeric film former.
52. The dental composition of claim 48 further comprising a hardenable resin.
53. The dental composition of claim 52, wherein the hardenable resin comprises acid functionality.
54. The dental composition of claim 53, wherein the acid functionality comprises carboxylic acid functionality, phosphoric acid functionality, phosphonic acid functionality, sulfonic acid functionality, or combinations thereof.
55. The dental composition of claim 52 further comprising an initiator system.
56. The dental composition of claim 52, wherein the hardenable resin comprises an ethylenically unsaturated compound.

57. The dental composition of claim 56, wherein the ethylenically unsaturated compound is selected from the group consisting of an ethylenically unsaturated compound with acid functionality, an ethylenically unsaturated compound without acid functionality, and combinations thereof.
58. The dental composition of claim 48, wherein the composition is selected from the group consisting of dental primers, dental adhesives, cavity liners, cavity cleansing agents, cements, coatings, varnishes, orthodontic adhesives, restoratives, sealants, desensitizers, and combinations thereof.
59. A method of treating a tooth structure comprising contacting the tooth structure with a dental composition according to claim 48.
60. A method of remineralizing a tooth structure comprising placing a dental composition according to claim 48 in an oral environment.
61. A method of reducing sensitivity of a tooth structure comprising placing a dental composition according to claim 48 in an oral environment.
62. A method of protecting a tooth structure comprising placing a dental composition according to claim 48 in an oral environment.
63. A method of delivering ions to an oral environment comprising:  
placing a dental composition according to claim 48 in the oral environment, wherein the ions comprise elements selected from the group consisting of calcium, phosphorus, fluorine, and combinations thereof.
64. A method of preparing a dental article comprising:  
combining a dental filler according to claim 1 and a hardenable resin to form a dental composition; and

hardening the composition to fabricate a dental article selected from the group consisting of crowns, fillings, mill blanks, orthodontic devices, and prostheses.

65. A dental composition comprising:

- a dental filler according to claim 1;
- a hardenable resin; and
- a water-dispersible, polymeric film former.

66. The dental composition of claim 65, wherein the hardenable resin and the water-dispersible, polymeric film former are the same.

67. The dental composition of claim 65, wherein the hardenable resin and the water-dispersible, polymeric film former are different.