



Office de la Propriété

Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2587278 A1 2006/05/26

(21) **2 587 278**

(12) **DEMANDE DE BREVET CANADIEN**
CANADIAN PATENT APPLICATION

(13) **A1**

(86) Date de dépôt PCT/PCT Filing Date: 2005/11/07
(87) Date publication PCT/PCT Publication Date: 2006/05/26
(85) Entrée phase nationale/National Entry: 2007/05/10
(86) N° demande PCT/PCT Application No.: US 2005/040340
(87) N° publication PCT/PCT Publication No.: 2006/055328
(30) Priorité/Priority: 2004/11/16 (US10/989,523)

(51) Cl.Int./Int.Cl. *A61K 6/027*(2006.01),
A61K 6/083(2006.01)

(71) **Demandeur/Applicant:**
3M INNOVATIVE PROPERTIES COMPANY, US

(72) **Inventeurs/Inventors:**
RUSIN, RICHARD P., US;
MITRA, SUMITA B., US;
CUMMINGS, KEVIN M., US;
BURGIO, PAUL A., US;
FALSAFI, AFSHIN, US

(74) **Agent:** SMART & BIGGAR

(54) Titre : CHARGES DENTAIRES, PROCEDES, COMPOSITIONS INCLUANT UN CASEINATE

(54) Title: DENTAL FILLERS, METHODS, COMPOSITIONS INCLUDING A CASEINATE

(57) Abrégé/Abstract:

The present application provides dental fillers, and methods of making and using dental fillers that include a treated surface that includes a caseinate. Dental compositions including such dental fillers can be useful for delivering ions to the oral environment. Dental compositions, and methods of using dental compositions that include a caseinate and a hardenable resin or a water-dispersible, polymeric film former are also provided.



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
26 May 2006 (26.05.2006)

PCT

(10) International Publication Number
WO 2006/055328 A1(51) International Patent Classification:
A61K 6/027 (2006.01) A61K 6/083 (2006.01)

(74) Agents: EDMAN, Sean, J. et al.; 3M Center, Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(21) International Application Number:
PCT/US2005/040340

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(22) International Filing Date:
7 November 2005 (07.11.2005)

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(25) Filing Language:
English(26) Publication Language:
English(30) Priority Data:
10/989,523 16 November 2004 (16.11.2004) US

(71) Applicant (for all designated States except US): 3M INNOVATIVE PROPERTIES COMPANY [US/US]; 3m Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

- with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: DENTAL FILLERS, METHODS, COMPOSITIONS INCLUDING A CASEINATE

(57) **Abstract:** The present application provides dental fillers, and methods of making and using dental fillers that include a treated surface that includes a caseinate. Dental compositions including such dental fillers can be useful for delivering ions to the oral environment. Dental compositions, and methods of using dental compositions that include a caseinate and a hardenable resin or a water-dispersible, polymeric film former are also provided.

WO 2006/055328 A1

DENTAL FILLERS, METHODS, COMPOSITIONS INCLUDING A CASEINATE

5

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.

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

SUMMARY OF THE INVENTION

In one aspect, the present invention provides a dental filler including a treated surface, and methods of making and using such a dental filler including a treated surface. The treated surface includes a caseinate, which preferably includes a salt of calcium, phosphate, fluoride, or combinations thereof. Dental compositions including such a dental filler, and methods of using such dental compositions are also provided.

In another aspect, the present invention provides a dental composition that includes a hardenable resin and/or a water-dispersible, polymeric film former; and a caseinate, wherein the caseinate is at least partially dissolved, suspended, or dispersed in the hardenable resin and/or water-dispersible, polymeric film former. Preferably, the

caseinate includes a salt of calcium, phosphate, fluoride, or combinations thereof.

Methods of using such dental compositions are also provided.

Dental fillers and compositions as disclosed herein preferably lead to enhanced 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.

10 *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.

20 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 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.

30 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.

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., 5 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, 10 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 15 "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 20 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.

25

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention provides dental fillers and/or compositions that include a caseinate. In some embodiments, a dental filler is provided that includes a treated surface that includes a caseinate. In some embodiments, dental compositions are provided that 30 include such dental fillers. In some embodiments, dental compositions are provided that include a caseinate 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.

CASEINATES

5 Casein is a mixture of related phosphoproteins occurring in milk and cheese. As used herein, "casein" is meant to include one or more of the major casein components, which can be distinguished by electrophoresis and are commonly designated as α -, β -, γ -, and κ -caseins, in order of decreasing mobility at pH 7. The complete amino acid sequence of bovine β -casein is known and contains 209 residues with an approximate molecular 10 weight of 23,600. See, for example, Ribadeaudumas et al., *Eur. J. Biochem.*, 25:505 (1972) and McKenzie, *Advan. Protein Chem.*, 22:75-135 (1967).

Casein is amphoteric and forms salts with both acids and bases. When both the cation and anion of a species (e.g., calcium phosphate) form salts with casein, the product is typically referred to as a complex (e.g., a calcium phosphate complex of casein. As 15 used herein, the term "caseinate" is used to refer to salts and/or complexes of a casein.

Typical caseinates include, for example, salts of monovalent metals (e.g., sodium and potassium), salts of divalent metals (e.g., magnesium, calcium, strontium, nickel, copper, and zinc), salts of trivalent metals (e.g., aluminum), ammonium salts, phosphate salts (e.g., phosphate and fluorophosphate), and combinations thereof. Typical caseinate complexes include, for example, calcium phosphate complexes (available under the trade 20 designation PHOSCAL from NSI Dental Pty.Ltd., Hornsby, Australia), calcium fluorophosphate complexes, calcium fluoride complexes, and combinations thereof.

Caseinates are typically available as dry powders. Caseinates may be either soluble or insoluble in aqueous fluids.

25

SURFACE TREATMENT OF DENTAL FILLERS

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 a liquid having 30 dissolved, dispersed, or suspended therein, a caseinate as described herein. The liquid or additional liquids may optionally include additional surface treating agents (e.g., fluoride ion precursors, silanes, titanates, etc). Optionally the liquid includes water, and if an

aqueous liquid is used, it can be acidic or basic. Once treated, at least a portion of the liquid 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 5 drying. In one embodiment, the treated fillers can be oven dried, typically at drying temperatures of about 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 incorporated, for example, into a dental paste.

10 Dental fillers suitable for surface treatment can be selected from one or more of a 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 15 nanoparticles. Preferred classes of fillers include metal oxides, metal fluorides, metal oxyfluorides, and combinations thereof, wherein the metal can be a heavy or non-heavy metal.

20 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 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 25 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.

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.

5 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 10 under the trade designations AEROSIL, including "OX 50," "130," "150" and "200" silicas 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-15 vitreous microparticles of the type described in U.S. Pat. No. 4,503,169 (Randklev). 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 20 metal oxides, glasses, and metal salts. Typical metal oxides include barium oxide, calcium 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 25 the hardenable composition. The glass also typically contains sufficient elutable fluoride 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 30 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 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 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.

Other suitable fillers are disclosed, for example, in U.S. Pat. Nos. 6,306,926 (Bretschler 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. 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 caseinate, 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 most 50%, more preferably at most 30%, and most preferably at most 20% by weight caseinate, 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 5 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., 10 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).

15

DENTAL COMPOSITIONS INCLUDING A CASEINATE

In some embodiments, the present invention provides dental compositions that include a caseinate and a hardenable resin and/or a water-dispersible, polymeric film former. Such dental compositions can be prepared either directly (e.g., by combining the 20 caseinate with the hardenable resin or the water-dispersible, polymeric film former) or indirectly (e.g., by generating the caseinate in the hardenable resin or a water-dispersible, polymeric film former *in situ*). Suitable *in situ* methods of generating the caseinate include, for example, neutralization reactions, complexation reactions, and/or ion exchange reactions.

25

Dental compositions that include a caseinate in a hardenable resin include, for example, dental adhesives, dental restoratives, and orthodontic adhesives. Dental compositions that include a caseinate in a water-dispersible, polymeric film former include, for example, coatings, varnishes, sealants, primers, and desensitizers. In some embodiments as described herein above, the caseinate is present in a surface treated filler. 30 In other embodiments, the caseinate is not present in a surface treated filler.

For embodiments in which a dental composition includes a caseinate in a hardenable resin, wherein the caseinate is not present in a surface treated filler, the dental

composition preferably includes at least 0.01%, more preferably at least 0.1%, and most preferably at least 1% by weight caseinate, based on the total weight of the dental composition. For such embodiments, the dental composition preferably includes at most 70%, more preferably at most 50%, and most preferably at most 25% by weight caseinate, 5 based on the total weight of the dental composition.

For embodiments in which a dental composition includes a caseinate in a water-dispersible, polymeric film former, wherein the caseinate is not present in a surface treated filler, the dental composition preferably includes at least 0.01%, more preferably at least 0.1%, and most preferably at least 1% by weight caseinate, based on the total weight of the 10 dental composition. For such embodiments, the dental composition preferably includes at most 70%, more preferably at most 50%, and most preferably at most 25% by weight caseinate, based on the total weight of the dental composition.

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

15 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 INCLUDING HARDENABLE RESINS

20 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 25 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 30 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

5 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, 10 α,β -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 15 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, 20 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 25 (meth)acrylated acids (e.g., methacrylated trimellitic acids), and anhydrides thereof can be 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 30 between isocyanatoalkyl (meth)acrylates and carboxylic acids. Additional compounds of this type having both acid-functional and ethylenically unsaturated components are 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. 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 5 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. Nos. 4,259,075 (Yamauchi et al.), 4,499,251 (Omura et al.), 4,537,940 (Omura et al.), 10 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 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.

15 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 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 20 60% by weight ethylenically unsaturated compounds with acid functionality, based on the total weight of the unfilled composition.

ETHYLENICALLY UNSATURATED COMPOUNDS WITHOUT ACID FUNCTIONALITY

25 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.

30 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.

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 5 compositions are sometimes referred to as "self-cure" compositions and may include glass ionomer cements, resin-modified glass ionomer cements, redox cure systems, and combinations thereof.

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 10 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.

15

Photopolymerizable Compositions

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 20 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 25 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 methacrylate, n-hexyl acrylate, stearyl acrylate, allyl acrylate, glycerol triacrylate, 30 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[l-(2-acryloxy)]-p-ethoxyphenyldimethylmethane, bis[l-(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 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 10 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 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-15 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 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.

20 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 25 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.

30 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 5 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 10 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, 15 3,3,6,6-tetramethylcyclohexanedione, phenanthraquinone, 1-phenyl-1,2-propanedione and other 1-aryl-2-alkyl-1,2-ethanediones, 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. 20 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 25 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 30 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 5 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.

10 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.

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

Chemically Polymerizable Compositions

The chemically polymerizable compositions may include redox cure systems that include a polymerizable component (e.g., an ethylenically unsaturated polymerizable 20 component) and redox agents that include an oxidizing agent and a reducing agent.

Suitable polymerizable components, redox agents, optional acid-functional components, 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.).

25 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 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 30 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 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 5 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.

10 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 15 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.

20 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 in U.S. Pat. Publication No. 2003/0195273 (Mitra et al.).

25 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.

30 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 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 5 than 5% by weight, based on the total weight (including water) of the components of the polymerizable composition.

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 10 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.

15 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.

20

WATER-DISPERSIBLE POLYMERIC FILM FORMER

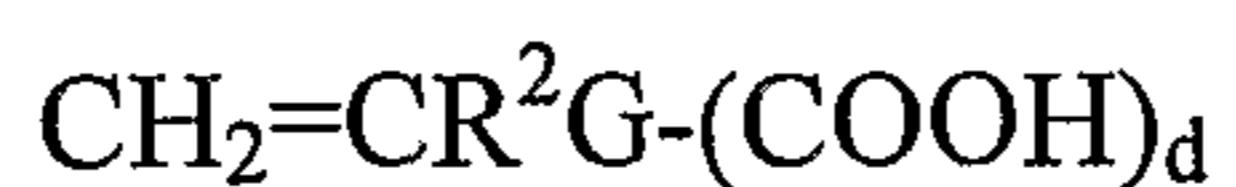
In some embodiments, water-dispersible polymeric film formers as disclosed herein include a repeating unit that includes a polar or polarizable group as described herein below. In certain embodiments, the water-dispersible polymeric film formers also 25 include a repeating unit that includes a fluoride 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 30 (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.).

Repeating units including a polar or polarizable group are derived from vinylic 5 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.

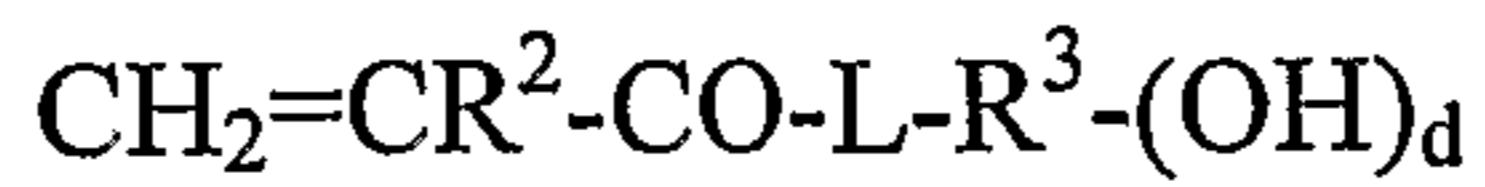
Examples of polar or polarizable groups include neutral groups such as hydroxy, thio, substituted and unsubstituted amido, cyclic ethers (such as oxanes, oxetanes, furans and pyrans), basic groups (such as phosphines and amines, including primary, secondary, 10 tertiary amines), acidic groups (such as oxy acids, and thooxyacids 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 follow.

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



20 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 25 N-acryloyl glycine.

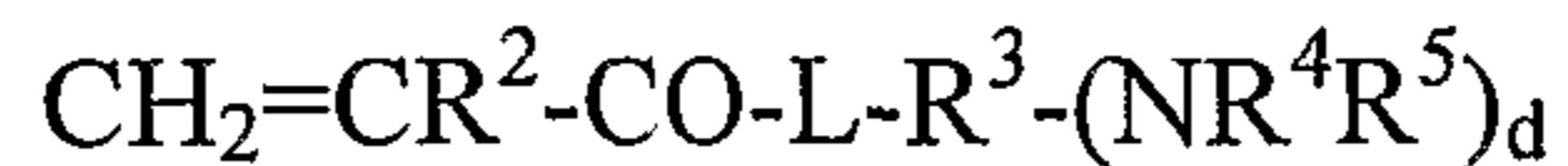
Polar or polarizable groups may, for example, be derived from mono- or multifunctional hydroxy group containing molecules represented by the general formula:



30 where $\text{R}^2=\text{H}$, methyl, ethyl, cyano, carboxy or carboxyalkyl, $\text{L}=\text{O, NH}$, $d=1-5$ and 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.

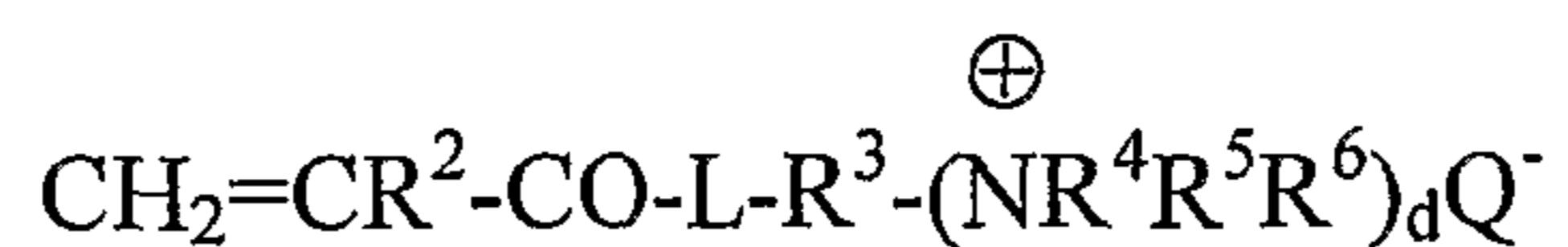
5 Polar or polarizable groups may alternatively be derived from mono- or multifunctional amino group containing molecules of the general formula:



10 where R^2 , L, R^3 , and d are as defined above and R^4 and 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.

15 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.

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



25 where R^2 , R^3 , R^4 , R^5 , L and d are as defined above, and where R^6 is H or alkyl of 1-12 carbon atoms and Q^{\ominus} is an organic or inorganic anion. Preferred examples of such 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 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 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 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 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 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 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.

5 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; ω -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

10 $\text{CF}_3(\text{CF}_2\text{CF}_2\text{O})_q(\text{CF}_2\text{O})_x(\text{CH}_2)_y\text{OH}$, 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.

15 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.

20 Monomers used to provide the graft polysiloxane chain of this invention are terminally functional polymers having a single functional group (vinyl, ethylenically 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 by Y. Yamashita et al., [Polymer J. 14, 913 (1982); ACS Polymer Preprints 25 (1), 245 (1984); Makromol. Chem. 185, 9 (1984)].

30 In certain embodiments, the water-dispersible polymeric film formers disclosed herein also include a repeating unit that includes a modulating group. Exemplary 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 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 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., 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.

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 5 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.

10 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.

15

EXAMPLES

Test Methods

Visual Opacity (MacBeth Values) Test Method

5 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
10 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.

Compressive Strength (CS) Test Method

15 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
20 (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
25 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.

30 Diametral Tensile Strength (DTS) Test Method

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 5 in MPa as the average of the five measurements.

Work Time (WT) Test Method

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 10 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 every 10 sec. The end of the working time was determined when the lumps of the cement 15 sample moved with the groove maker. The working time was reported as the average of 2 or 3 measurements.

20

Spectral Opacity (SO) Test Method

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 25 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 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 30 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 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.

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

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 For primer compositions, AD and AE were measured as above, except that the primer composition was swabbed on a moist bovine tooth surface for 20 sec, gently air-dried 5-10 sec, and then light-cured 10 sec; and Vitremer Core Restorative was used instead of the Filtek Z250 composite.

15 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 20 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 α_1/α_2 separation.

25

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 30 37°C; the solution was exchanged periodically, and the ion content measured via 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 the initial disk weight and by the time in days since the last exchange of buffer

5 solution.

Enamel 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. The demineralizing solution was 0.1 ppm F⁻ from NaF, 1.5 mM Ca⁺² from CaCl₂, 0.9mM PO₄⁻³ from KH₂PO₄, 50 mM acetic acid, adjusted to pH=5.0 with 1M KOH; and the mineral content was measured by quantitative image analysis of microradiographs.

15 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⁻ from NaF, 1.5 mM Ca⁺² from CaCl₂, 0.9mM PO₄⁻³ from KH₂PO₄, 50 mM acetic acid, adjusted to pH=5.0 with 1M KOH; and the mineral content was measured by quantitative image analysis of microradiographs.

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⁻ from NaF, 1.5 mM Ca⁺² from CaCl₂, 0.9mM PO₄⁻³ from KH₂PO₄, 50 mM acetic acid, adjusted to pH=5.0 with 1M KOH; and the extent of acid erosion adjacent to the sample was qualitatively categorized from microradiographs.

30

Abbreviations, Descriptions, and Sources of Materials

Abbreviation	Description and Source of Material
--------------	------------------------------------

BisGMA	2,2-Bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane CAS No. 1565-94-2
TEGDMA	Triethyleneglycol dimethacrylate (Sigma-Aldrich, St. Louis, MO)
PEGDMA-400	Polyethyleneglycol dimethacrylate (Sartomer 603; MW about 570; Sartomer, Exton, PA)
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 ρ = 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)

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	Silane-treated, 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. 657,572,693 (Wu et al.).
Filler E	Schott Glass Product No. G 018-117 (Schott Electronic Packaging, GmbH, Landshut, Germany). The filler was silane-treated as described for Filler FAS VI in U.S. Pat. Publication No. 2003/0166740 (Mitra et al.).
Filler F	Silane-treated nanozirconia prepared according to the procedure for Preparatory Example 1A in U.S. Pat. Application No. 10/847,781, filed May 17, 2004 (Kangas et al.)
Filler G	Silane-treated, non-aggregated, nano-sized silica particles in the form of a dry powder were prepared according to the procedure for Filler A in U.S. Pat. Publication No. 2003/0181541 (Wu et al.), except that Nalco 2327 was used in place of Nalco 2329. The nominal particle size of this filler was assumed to be the same as in the starting Nalco 2327 silica sol, i.e., about 20 nanometers.

Filler H	Silane-treated, non-aggregated, nano-sized silica particles in the form of a dry powder were prepared according to the procedure for Filler A in U.S. Pat. Publication No. 2003/0181541 (Wu et al.). The nominal particle size of this filler was assumed to be the same as in the starting Nalco 2329 silica sol, i.e., about 75 nanometers.
PHOSCAL	Caseinate material comprising a casein phosphoprotein-calcium phosphate complex. (NSI Dental, Australia)
Sodium Caseinate	Sodium salt of casein comprising a calcium phosphate complex (ICN Biomedicals, Aurora, OH)
Nalco 1042	Acidic colloidal silica sol (Nalco Corp., Naperville, IL)
Nalco 2329	Sodium hydroxide stabilized colloidal silica sol (Nalco Corp.)
Nalco 2326	Colloidal silica sol (Nalco Corp.)
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 resin component of VITREMER Restorative (3M Company)
Vitremer Primer	Liquid primer component packaged with VITREMER Core Build-Up/Restorative (3M Company)
Filtek Z250 Resin	Resin component of FILTEK Z250 Universal Restorative System (3M Company)
F2000 Resin	Resin component of F2000 Compomer Restorative System (3M Company)
AC-315	AVALURE acrylate-based copolymer (Noveon, Inc., Cleveland, OH)
940NF	CARBOPOL carbomer-based polymer (Noveon, Inc.)
UR-450	AVALURE urethane polymer (Noveon, Inc.)

Starting Materials Preparations

6-Methacryloyloxyhexyl Phosphate (MHP)

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 Na₂SO₄ 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 P₄O₁₀ (178.66 g, 0.63 mol) and methylene chloride (500 ml) in a 1-liter flask equipped with a mechanical stirrer under N₂ 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.

30 Resins A, B, C, D and E

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

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

Ingredient (Weight %)	Resin A	Resin B	Resin C	Resin D	Resin E
VBP	43.43	43.00	0	0	0
HEMA	22.27	22.05	17.00	0	0
BisEMA6	0	0	0	32.00	37.13
BisGMA	0	0	27	0	0
TEGDMA	0	0	38	32.00	60.00
MHP	0	0	14.34	0	0
PM-2	0	0	0	33.15	0
Water	34.04	33.70	0	0	0
CPQ	0.30	0.30	0.32	0.3	0.3
DPIHFP	0	1.00	0.53	0	0
BHT	0.05	0.05	0.39	0.15	0.17
EDMAB	0	0	2.42	2.4	2.4
TOTAL:	100	100	100	100	100

Examples 1A and 1B

Zirconia-Silica Nanocluster Fillers Treated with Caseinate Materials 5

Example 1A. Filler B (nanocluster zirconia-silica) (149.3 g) was stirred into a solution of 10% by weight Sodium Caseinate (213.4 g) to form a smooth, creamy slurry. To this slurry was added sequentially a solution of 10% by weight Na_2HPO_4 in deionized water (35.4 g); additional deionized water (57 g); a solution of 3.9% by weight NaOH in deionized water (57 g) to adjust the Ph from about 6.5 to about 9.0; and a solution of 46.4% by weight $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in deionized water (35.4 g) to yield a homogeneous dispersion with no gelation or settling. This dispersion was dried on a gap dryer to yield thin flakes approximately 2-10 mm across, which were extremely friable and readily crushed to a fine powder (designated Example 1). The final powder had a calculated composition of 20% calcium-phosphate-caseinate and 80% Filler B. Powder X-Ray

Diffraction (XRD) showed that the powder was largely amorphous, with peaks for NaCl (crystallite size \geq 1500 Å, relative peak size 100) and monoclinic zirconia (crystallite size 30 Å, relative peak size 36). For comparison, the XRD pattern of the as-received Sodium Caseinate showed a notable difference in the shape of the broad amorphous peaks. The

5 Sodium Caseinate had a major broad peak at $d = 4.3778$ Å and an additional broad peak at $d = 9.4020$ Å, possibly indicative of a disordered crystalline structure. Example 1A, by contrast, had a major broad peak at $d = 3.8415$ Å (significantly shifted compared to the Sodium Caseinate), and no peaks at higher d -spacings; this pattern is indicative of an amorphous material.

10 Example 1B. Filler B (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 1B) contained 10% PHOSCAL and 90% Filler B.

15

Examples 2A-2C

Silica Nanocluster Fillers Treated with Caseinate Materials

Example 2A. Nalco 2329 colloidal silica sol (89.6 g) was stirred into a solution of 10% by weight Sodium Caseinate (213.4 g) to form a thin, turbid sol. To this sol was added sequentially a solution of 10% by weight Na_2HPO_4 in deionized water (28.0 g); a solution of 3.9% by weight NaOH in deionized water (9.7 g) to adjust the Ph from about 7.4 to about 9.5; and a solution of 46.4% by weight $CaCl_2 \cdot 2H_2O$ in deionized water (7.2 g). After a short period of time, some white gelatinous globs appeared. This sol was refrigerated overnight, and then dried on a gap dryer the next day to yield thin flakes which were extremely friable and readily crushed to a fine powder (designated Example 2A). The white precipitates caused some difficulties in the gap dryer.

Example 2B. Nalco 2329 colloidal silica sol (154 g) was stirred into a solution of 10% by weight Sodium Caseinate (213.4 g) to form a thin, turbid sol. To this sol was added sequentially a solution of 10% by weight Na_2HPO_4 in deionized water (9.8 g); a solution of 3.9% by weight NaOH in deionized water (7.0 g) to adjust the Ph from about 7.4 to about 9.5; and a solution of 46.4% by weight $CaCl_2 \cdot 2H_2O$ in deionized water (2.5 g) to yield a stable, homogeneous sol with no precipitates, separation, or gelation. This sol was refrigerated overnight, and then dried on a gap dryer the next day to yield large, thin

flakes which were extremely friable and readily crushed to a fine powder (designated Example 2B). XRD showed that the powder was largely amorphous, with peaks only for NaCl (crystallite size 1305 Å) evident. There was a single major broad peak at $d \sim 4.0 \text{ \AA}$, with no peaks at higher d -spacings; this XRD pattern was similar to the XRD pattern for Example 1A. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) images of Example 2B showed that the spherical colloidal silica particles were bound together in clusters by the caseinate.

Example 2C. PHOSCAL (6.0 g) was dissolved into Nalco 2326 colloidal silica (92.2 g) to form a thin, homogeneous, slightly turbid sol. The sol was gap-dried on the same day, yielding coarse, friable granules whose net composition was 30% PHOSCAL and 70% silica. The granules were friable and readily crushed to a fine powder (designated Example 2C). Powder XRD of PHOSCAL revealed a broad peak structure (at about $d \sim 4.3 \text{ \AA}$ and $d \sim 9.6 \text{ \AA}$) similar to the XRD pattern for Sodium Caseinate (see Example 1A), with additional nanocrystalline peaks at $d = 2.8 \text{ \AA}$ from NaCl, and at $d = 3.4 \text{ \AA}$ that might be a calcium phosphate phase. Example 2C, by contrast, had a broad peak at $d \sim 3.9 \text{ \AA}$, and a very small peak at $d \sim 9.8 \text{ \AA}$ (much smaller than in the PHOSCAL pattern). The broad peak at $d = 2.8 \text{ \AA}$ (NaCl) was much smaller in the Example 2C pattern than in the PHOSCAL pattern and there were no peaks at about $d = 3.4 \text{ \AA}$.

20

Example 3
Oven-Dried Caseinate (PHOSCAL)

A solution of 12% PHOSCAL in deionized water was dried in a glass tray at 100°C for 3 hours. In another experiment, the PHOSCAL solution was dried as above and then further heated at 140°C for 15 hours. XRD patterns of the as-received, dried, and dried/heated PHOSCAL powder materials had the same broad peak structure (peaks at about $d \sim 4.3 \text{ \AA}$ and $d \sim 9.6 \text{ \AA}$). Moreover, the XRD pattern for the dried material lacked the nanocrystalline peak at $d = 3.4 \text{ \AA}$ ($\theta \sim 28^\circ$); this peak is present in the XRD pattern for the dried/heated material which was heated at higher temperatures for much longer times. Thus, conventional oven drying did not impart the unique structure seen in the inventive materials (e.g. Examples 1A and 2C), which lacked the broad peak at $d \sim 9.6 \text{ \AA}$. These

experiments demonstrate that the inventive processes can impart a unique structure to the caseinate materials.

PHOSCAL – General Solubility Properties

5 PHOSCAL dissolved readily in water at up to 16% by weight to form a cloudy, stable solution; at 16% a thick liquid was formed; and at 20% a soft gel was formed.

PHOSCAL dispersed into, but did not dissolve in ethanol or in certain methacrylate resins (e.g., HEMA, FILTEK Z250 resin, and certain resins containing phosphorylated components).

10 PHOSCAL was mixed into ethanol at 0.1%, 1.0%, 2.0%, and 8.0% with essentially no solubility observed. After 7 months aging under ambient conditions, the PHOSCAL readily dispersed within the ethanol with agitation. Similar results were observed for PHOSCAL in a methacrylate resin (FILTEK Z250 resin) at 0.1% to 4.0% and in HEMA at 2.0%.

15 PHOSCAL at 6.2% blended into an 80/20 ethanol/deionized water (DIW) solution to form a white, gelatinous lump. However, PHOSCAL at 8% solution in DIW (0.8 g) blended with ethanol (1.0 g) to form a cloudy, stable solution. Thus the order of addition affected the solubility results in some cases.

20

Examples 4A-4F

Glass Filler Treated with Caseinate Materials

Vitrebond Powder (glass filler) was slurried with ethanol followed by the addition of a caseinate material and the resulting mixture blended thoroughly to form a creamy, homogeneous slurry. The slurry was either gap-dried or dried in a PYREX tray at 80°C for 25 4 hours in a convection oven. The compositions prepared and observations of the dried materials are provided in Table 2.

Table 2

Example	Caseinate %	Drying Method	Comment
4A	1% Phoscal	Tray-dried	Friable cake, easily crushed to powder

4B	5% Phoscal	Tray-dried	Friable cake, easily crushed to powder
4C	5% Sodium Caseinate	Tray-dried	Friable cake, easily crushed to powder
4D	10% Phoscal	Tray-dried	Hard cake, crushed in mortar & pestle to powder
4E	2% Phoscal	Tray-dried	Friable cake, easily crushed to powder
4F	10% Phoscal	Gap-dried	Friable flakes

Examples 5A-5B and Comparative Examples (CE) 1-3

Stability of Silica Nanoparticles Treated with a Caseinate Material (PHOSCAL)

The stability of compositions containing VBP, colloidal silica (Nalco 1042), and PHOSCAL (Examples 5A-5B) were compared to similar compositions that lacked either the colloidal silica or the PHOSCAL (Comparative Examples 1-3). The PHOSCAL, if present, was first dissolved in the water before blending into the final composition. All compositions were aged in glass vials under ambient conditions. The compositions (values are weight %) and observations at 7-months ageing are provided in Table 3. Only the compositions containing both colloidal silica nanoparticles and PHOSCAL were found to be stable at 7 months.

In a separate experiment, the sodium monofluorophosphate (Na_2FPO_3) was shown to cause the Nalco 1042 to gel. Thus, the presence of the caseinate material PHOSCAL appeared to stabilize the Nalco 1042 in the presence of the sodium monofluorophosphate.

In another experiment, varying levels of PHOSCAL (0.1, 1, 2, and 4%) were mixed into a solution of 50% VBP, 40% EtOH, 10% Nalco 1042 to form cloudy solutions. All solutions remained as homogeneous, cloudy, and stable through 7 months under ambient conditions.

Table 3

Example	VBP	EtOH	DI	Nalco	PHOSCAL	Na_2FPO_3	Appearance at

			Water	1042			7 months
5A	41.7	33.3	14.7	8.3	2	0	Homogeneous; no precipitation, gelation, separation
CE 1	45.3	36.3	7.9	9.1	0	1.5	Separation; rubbery gel
CE 2	44.9	35.9	18.0	0	1.2	0	Separation
CE 3	45.2	36.2	17.1	0	0	1.6	Separation; rubbery gel
5B	43.5	34.8	11.3	8.7	1	0.7	Homogeneous; no precipitation, gelation, separation

Examples 6-13 and Comparative Examples 4-5

RMGI Compositions Containing a Caseinate (PHOSCAL)

The caseinate material PHOSCAL (included in Powder 2) was mixed with

5 Vitrebond Powder (Powder 1 or Powder 2 component) and then with various liquid resins to afford homogeneous RMGI pastes designated Examples 6-13. These pastes were evaluated for compressive strength (CS), diametral tensile strength (DTS), work time, spectral opacity, and adhesion to dentin (AD) according to the Test Methods described herein and the results compared to those from the commercial VITREBOND (VB) Light

10 Cure Glass Ionomer Liner/Base product (Comparative Examples (CE) 4 and 5). (For the AD 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 4A and the evaluation results in Table 4B.

Table 4A

Example	Powder 1 (P1)	Powder 2 (P2)	Liquid Resin (L)	P1/P2/L (Weight Ratio)
CE 4	Vitrebond	None	Vitrebond	1.4/0/1
CE 5	Vitrebond	None	Vitrebond	1/0/1
6		Example 4A	Resin B	0/1/1
7		Example 4E	Resin B	0/1/1
8	Vitrebond	PHOSCAL	Vitrebond	.95/.05/1
9		Example 4B	Vitremer	0/1/1
10	Vitrebond	Example 1B	Resin B	0.5/0.5:/1
11		Example 4F	Resin B	0/1/1
12		Example 4D	Resin B	0/1/1
13	Vitrebond	Example 2C	Resin B	0.9/ 0.1/1

Table 4B

Example	Spectral Opacity	CS MPa (SD)	DTS MPa (SD)	Work Time Min:Sec	Dentin Adhesion MPa (SD)
CE 4	77.19	113 (9.5)	25.3 (1.7)	4:55	6.9 (5.6)
CE 5	80.60	104 (3)	19.8 (4.2)	5:05	NT*
6	78.05	88 (7)	17.3 (3.1)	5:05	9.7 (1.7)
7	NT	84 (15)	15.9 (2.7)	NT	9.5 (1.2)
8	NT	65 (5)	11.6 (1.6)	NT	NT
9	76.14	57 (5)	10.8 (1.1)	5:00	6.0 (2.7)
10	74.22	86 (7)	15.8 (1.6)	NT	6.9 (1.6)
11	72.51	36 (4)	5.3 (1.0)	4:40	4.1 (0.9)
12	74.59	51 (3)	10.4 (1.4)	4:40	1.2 (1.3)
13	72.62	91 (11)	15.0 (1.2)	NT	NT

*NT – Not Tested

Examples 14-16

Acidic Resin Compositions Containing a Caseinate (PHOSCAL)

Acidic resin compositions containing a caseinate (PHOSCAL) (Examples 14-16) were prepared by combining the ingredients shown in Table 5. The resulting paste compositions were evaluated for compressive strength (CS), diametral tensile strength (DTS), spectral opacity, and shear adhesion to dentin and enamel according to the Test Methods described herein and the results are provided in Table 5.

Table 5

Example	Composition (Numbers are Weight %)	Spectral Opacity	CS MPa (SD)	DTS MPa (SD)	Dentin Adhesion MPa (SD)	Enamel Adhesion MPa (SD)
14	Resin D - 42 PHOSCAL - 8 Filler C - 15 Filler D - 35	51.46	183 (49)	27.7 (9.1)	3.1 (1.3)	17.5 (5.7)
15	Resin D - 45 Filler C - 15 Example 1B - 40	66.48	192 (36)	39.6 (4.7)	NT	NT
16	Resin D - 38 Filler C - 15 Filler D - 35 Example 2C - 12	60.46	215 (39)	27.6 (14.1)	NT	NT

Acidic Resin Compositions Containing a Caseinate Material

Acidic resin compositions containing a caseinate material were prepared by combining the ingredients listed below. The resulting paste compositions were evaluated in calcium and phosphorus ion release evaluations.

5 Example 17: Example 1A (55%), Vitremer Resin (45%)

Example 18: Example 1A (55%), Resin C (45%)

Example 19: Example 2B (55%), Vitremer Resin (45%)

Examples 20-22

10 Resin Compositions Containing a Caseinate (PHOSCAL)

PHOSCAL was soluble and stable in Resin B up to at least 16% by weight. The cloudiness and viscosity of the resulting resin increased with concentration. At less than 4%, the viscosity increase is minimal; at 8% the resin was much more viscous; and, at 16%, the resin was gelatinous. PHOSCAL in Resin B at 1%, 4% and 8% were designated 15 Examples 20-22, respectively. PHOSCAL exhibited similar behavior in Vitremer Resin. All of the resulting resins remained stable through at least 7 months at ambient conditions and would be suitable for a variety of applications, including RMGI materials, adhesives, primers, and coatings.

20 Examples 23-25 and Comparative Examples 6-7

RMGI Compositions Containing a Caseinate (PHOSCAL)

Liquid resin (Resin B) compositions containing PHOSCAL (Examples 20-22) were spatulated with Vitrebond Powder at a Powder/Liquid (P/L) ratio of 1.2/1 to afford homogeneous RMGI pastes designated Examples 23-25, respectively. These pastes were 25 evaluated for compressive strength (CS), diametral tensile strength (DTS), work time, spectral opacity, and adhesion to dentin (AD) according to the Test Methods described herein and the results compared to those from the commercial VITREBOND Light Cure Glass Ionomer Liner/Base product (Comparative Examples (CE) 6 and 7). (For the AD 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 data are provided in Table 6 and show 30 that the physical properties of the PHOSCAL (1%)-containing RMGI compositions were

generally the same as for the commercial VITREBOND product, whereas the PHOSCAL (4% and 8%)-containing RMGI compositions showed significantly lower strength values.

Table 6

Ex.	Powder	Liquid	P/L	Spectral Opacity	CS MPa (SD)	DTS MPa (SD)	Work Time Min:Sec	Dentin Adh. MPa (SD)
23	Vitrebond	Ex. 1 (1% PHOSCAL)	1.2/1	76.2	99 (5)	19.0 (4)	NT*	5.7 (1.0)
24	Vitrebond	Ex. 2 (4% PHOSCAL)	1.2/1	78.7	49 (4)	8.2 (1)	4.45	10.4 (3.6)
25	Vitrebond	Ex. 3 (8% PHOSCAL)	1.2/1	76.4	34 (9)	NT	NT	NT
CE 6	Vitrebond	Vitrebond	1.4/1	77.2	113 (10)	25.3 (1.7)	4:55	6.9 (5.6)
CE 7	Vitrebond	Vitrebond	1/1	80.6	104 (3)	19.8 (4.2)	5.05	NT

*NT – Not Tested

Table 7 provides the composition (weight % of ingredients) of aqueous polymerizable resin compositions containing PHOSCAL (Examples 26-29). These compositions were evaluated as primers for Vitremer Core Build-up/Restorative according to the Test Method described herein and the results (adhesion to dentin and enamel) 5 compared to those from the commercial Vitremer Primer product (Comparative Example 8). (For the AE and AD tests of these materials, the primer was brushed on the tooth surface for 20 sec, gently air-dried for 10 sec, and then light-cured for 10 sec.) The data are provided in Table 8 and show that the compositions containing PHOSCAL had adhesion values approximately equivalent to Vitremer Primer.

Resin Compositions Containing PHOSCAL (Ingredients in Weight %)						
Ex.	VBP	HEMA	EtOH	DIW	Nalco 1042	PHOSCAL
26	35	10	26	16	3	4
27	14	37	31.75	14.08	0	1.9
28	14	33.75	30	14.08	0	1.9
29	35	12	29.7	15	0	2
						5

Table 8

Example	Dentin Adhesion		Enamel Adhesion	
	MPa	SD	MPa	SD
CE 8	9.9	5.3	8.9	1.6
26	5.4	1.2	5.2	2.8
27	6.9	3.2	8.1	1.5
28	6.9	3.0	8.7	2.0
29	7.4	1.2	5.3	1.9

5

Examples 30-32 and Comparative Example 9

Adhesive Compositions Containing a Caseinate (PHOSCAL)

Example 21 (Resin B + 4% PHOSCAL) and Examples 28-29 were used as the Liquid B component in ADPER PROMPT L-POP Self-Etch Adhesive product (3M Company) and the resulting compositions evaluated for adhesion to enamel (AE) according to the Test Method described herein and the results compared to those for the commercial ADPER Adhesive product (Comparative Example (CE) 9). (For the AE tests of these materials, liquid A and B were mixed in a well; the adhesive was brushed onto the tooth surface for 20 sec, gently air-dried for 10 sec; and then light-cured for 10 sec.) The data are provided in Table 9.

Table 9

Example	Composition		Droplets	Enamel Adhesion MPa (SD)
	Liquid A	Liquid B		
CE 9	ADPER Product	ADPER Product	1:1	11.9 (2.3)
30	ADPER Product	Example 21	1:1	10.1 (2.7)
31	ADPER Product	Example 28	1:1	9.7 (4.5)
32	ADPER Product	Example 29	1:1	11.3 (4.1)

Examples 33-37

5 Tooth Coating Compositions Containing a Caseinate (PHOSCAL)

PHOSCAL was mixed at 1%, 2%, 4%, and 8% by weight into a solution of 50% VBP, 40% ethanol, and 10% DIW. After 7 months at ambient conditions, the 1%, 2%, and 4% samples showed sediment and separation, while the 8% composition (designated Example 33) remained homogeneous, 10 gelatinous, and stable.

PHOSCAL was mixed at various concentrations into a solution containing different film-forming polymers. The various compositions and their appearance are provided in Table 10. All of these compositions formed a hard, translucent-to-cloudy coating when dried onto a glass slide.

Table 10

Coating Compositions Containing PHOSCAL (Ingredients in Weight %)

Ex.	Polymer	PHOSCAL	Na ₂ FPO ₃	DIW	EtOH	Appearance
34	AC-315 - 22.5	9	16	0	52.5	Dispersible sediment
35	940NF - 1.5	10	5	83.5	0	Cloudy, homogeneous, stable gel
36	UR-450 - 90	1.2	0	8.8	0	Opaque, homogeneous, stable
37	UR-450 - 65.6	2.4	0	18	14	Opaque, homogeneous, stable

Examples 38-44

5 Methacrylate Resin Compositions Containing a Caseinate (PHOSCAL)

Methacrylate light-curable resin compositions containing PHOSCAL

(Examples 38-44) were prepared by combining the ingredients shown in Table 11. The paste compositions were evaluated for compressive strength, diametral tensile strength, spectral opacity, and adhesion to dentin (AD) and enamel (AE) according to the Test Methods described herein and the results are provided in Table 11. (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.)

Table 11

Example	Composition (Numbers are Weight %)	Spectral Opacity	CS MPa (SD)	DTS MPa (SD)	Dentin Adhesion MPa (SD)	Enamel Adhesion MPa (SD)
38	PHOSCAL - 4 Resin C - 50 Filler B - 45	54.4	273 (14)	53.7 (2.3)	0.00 (0.00)	8.1 (0.8)
39	PHOSCAL - 10 Resin E - 40 Filler C - 15 Filler D - 35	66.5	192 (36)	39.6 (4.7)	NT	3.0 (1.1)
40	PHOSCAL - 10 F2000 Resin - 40 Filler C - 15 Filler D - 35	60.5	215 (39)	27.6 (14.2)	NT	3.5 (0.96)
41	PHOSCAL - 8 Resin C - 42 Filler C - 15 Filler D - 35	56.4	169 (24)	34.6 (8.8)	10.6 (3.4)	12.0 (2.4)
42	PHOSCAL - 8 Resin D - 42 Filler C - 15 Filler D - 35	51.5	183 (49)	27.7 (9.1)	3.0 (1.3)	17.5 (5.7)
43	Resin D - 45 Filler C - 15 Example 1B - 40	45.7	180 (52)	28.3 (8.7)	NT	NT

44	Resin D - 38 Filler C - 15 Filler D - 35 Example 2C - 12	50.3	186 (13)	21.7 (3.3)	NT	NT
----	--	------	-------------	---------------	----	----

Example 45 and Comparative Example 10

Self-Adhesive Composition Containing a Caseinate (PHOSCAL)

PHOSCAL (5% by weight; 0.03625 g) was added to the powder component of RelyX Unicem Cement in a MAXICAP capsule (3M Company) and then mixed in a ROTOMIX mixer for 10 seconds to afford a paste that was designated Example 45. Example 45 was evaluated for compressive and diametral tensile strengths according to the Test Methods described herein and the results compared to those for the commercial RelyX Unicem Maxicap Self-Adhesive Universal Resin Cement product (Comparative Example (CE) 10). The data are provided in Table 12 and show that the physical properties of the PHOSCAL-containing cement composition were basically the same as for the commercial RelyX Unicem cement.

Table 12

Example	Composition	Compressive Strength MPa (SD)	Diametral Tensile Strength MPa (SD)
45	RelyX Unicem + PHOSCAL (5%)	197 (32)	52.3 (3.5)
CE 10	RelyX Unicem	199 (20)	51.8 (13.9)

15

Example 46 and Comparative Example 11

Paste-Paste RMGI System Containing a Caseinate (PHOSCAL)

PHOSCAL was added to the Paste B component of a Paste A/Paste B RMGI System and compared to the corresponding RMGI System without added

PHOSCAL. The compositions of Paste A and the two Paste B components are shown in Tables 13A and 13B.

Table 13A
Paste A Composition

Ingredient	Concentration (Weight %)
HEMA	2.05
PEGDMA-400	7.35
bisGMA	2.56
CPQ	0.1
EDMAB	0.11
Filler G	16.7
Filler E	41.01
Filler F	30.12
TOTAL:	100

Table 13B
Paste B Compositions

Ingredient	Concentration (Weight %)	
	Paste B1	Paste B2
DIW	13.68	13
PHOSCAL	0	2.11
HEMA	5.35	5.09
BHT	0.02	0.02
VBP	24.87	23.67
DPIHFP	0.14	0.13
Filler H	28	28
Filler D	28	28
TOTAL:	100	100

Paste A was combined with Paste B1 (Comparative Example 11) and Paste A was combined with Paste B2 (Example 46; with PHOSCAL). The two blended pastes were evaluated for visual opacity (Macbeth values) and adhesion to dentin and enamel (without primer) according to the Test Methods described 5 herein and results are provided in Table 13C.

Table 13C		
Test Results		
Test	CE 11	Example 46
Visual Opacity	0.33	0.32
Dentin Adhesion (MPa)	5.4	5.1
Enamel Adhesion (MPa)	2.6	5.6

Calcium and Phosphorus Ion Release Evaluations

Examples 6, 9-12, 17-19, 23-25, and 40 were evaluated for calcium and phosphorus release over time according to the Test Method described herein. 10 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 14.

Table 14: 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-E	ICP	Ca-E	ICP	Ca	P	Ca	ICP	Ca	P	Ca	ICP	Ca-E	Ca	Ca
6	NT	NT	3.17	NT	NT	3.56	NT	NT	NT	3.72	NT	NT	NT	NT	NT	0.91
9	NT	NT	2.66	NT	NT	2.76	NT	NT	NT	3.79	NT	NT	NT	NT	NT	6.33
10	NT	NT	1.87	NT	NT	2.72	NT	NT	NT	3.92	NT	NT	NT	NT	NT	3.17
11	NT	NT	2.30	NT	NT	3.16	NT	NT	NT	3.33	NT	NT	NT	NT	NT	3.30
12	NT	NT	2.26	NT	NT	2.01	NT	NT	NT	2.44	NT	NT	NT	NT	NT	2.95
17	178.1	301.7	NT	17.12	29.24	NT	NT	NT	NT	6.89	NT	NT	NT	NT	NT	0.48
18	NT	NT	19.17	NT	NT	4.58	NT	NT	NT	1.94	NT	NT	NT	NT	NT	1.45
19	NT	NT	NT	12.65	43.05	NT	NT	NT	NT	2.02	NT	NT	NT	NT	NT	0.21
23	NT	NT	1.96	NT	NT	2.69	NT	NT	NT	3.13	NT	NT	NT	NT	NT	NT
24	NT	NT	2.08	NT	NT	2.38	NT	NT	NT	3.22	NT	NT	NT	NT	NT	1.26
25	NT	NT	1.53	NT	NT	3.79	NT	NT	NT	3.48	NT	NT	NT	NT	NT	NT
40	NT	NT	2.62	NT	NT	0.81	NT	NT	NT	0.79	NT	NT	NT	NT	NT	NT

Dentin Remineralization Evaluations

Examples 4 (Vitrebond Powder treated with 5% PHOSCAL) and Example 24 were evaluated for dentin remineralization according to the Test Method described herein and showed remineralization after 3 weeks adjacent to and underneath the applied material in the area of the exposed lesion.

Enamel Remineralization Evaluations

Example 41 was evaluated for enamel remineralization according to the Test Method described herein. After 3 weeks storage in an artificial saliva solution, the samples were sliced and optical micrographs taken. In some images, new mineral formation was visible as bright white regions under the material within the lesion. New mineral formation was not seen in the areas exposed to the artificial saliva.

15

Resistance to Demineralization in Dentin Evaluations

Example 4A (Vitrebond Powder treated with 1% PHOSCAL), Example 10 (RMGI composition containing PHOSCAL) and comparative Examples 1 and 5 (VITREBOND Light Cure Glass Ionomer Liner/Base and FILTEK Z250 Universal Restorative System, respectively) were evaluated for resistance to demineralization in dentin according to the Test Method described herein. The resulting microradiographs and associated data (Table 15) showed that the VITREBOND product enhanced resistance to acid attack versus FILTEK Z250 and that Examples 4A and 10 enhanced this resistance dramatically.

Table 15				
Percent of Samples in Each Lesion Category				
Lesion Category	VITREBOND	Z250	Ex. 4A	Ex. 10
Full Lesion	27.3	100.0	8.3	10.5
Lesion thinner near material	33.3	0.0	25.0	31.6
Intact dentin near material, lesion farther away	39.4	0.0	66.7	57.9
No lesion discernible	0.0	0.0	0.0	0.0

Various modifications and alterations to this invention will become apparent to
5 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 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

15

What is claimed is:

1. A dental filler comprising a treated surface, wherein the treated surface comprises a caseinate.
2. The dental filler of claim 1, wherein the caseinate comprises a salt of calcium, phosphate, fluoride, or combinations thereof.
3. The dental filler of claim 1 wherein the treated surface is amorphous.
4. The dental filler of claim 1 wherein the treated surface is at least partially crystalline.
5. The dental filler of claim 1, wherein the dental filler is porous.
6. The dental filler of claim 5, wherein the porous dental filler is selected from the group consisting of porous particles, porous agglomerates of particles, and combinations thereof.
7. The dental filler of claim 1, wherein the dental filler comprises nanoparticles, agglomerates of nanoparticles, or combinations thereof.
8. The dental filler of claim 1, wherein the dental filler comprises metal oxides, metal fluorides, metal oxyfluorides, or combinations thereof.
9. The dental filler of claim 8, wherein the metal is selected from the group consisting of heavy metals, non-heavy metals, and combinations thereof.
10. 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.

11. The dental filler of claim 10, 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.
12. The dental filler of claim 1, wherein the dental filler comprises a glass, an amorphous material, or a crystalline material.
13. The dental filler of claim 1, wherein the dental filler comprises a source of fluoride ions.
14. The dental filler of claim 13, wherein the dental filler comprises a fluoroaluminosilicate glass.
15. The dental filler of claim 1, wherein the treated surface further comprises a silane.
16. The dental filler of claim 1, wherein the treated surface further comprises a source of fluoride ions.
17. The dental filler of claim 1, wherein the treated surface further comprises an antibacterial agent.
18. The dental filler of claim 1, wherein the treated surface further comprises Sr, Mg, Zn, Sn, Ag, or combinations thereof.
19. A method of making a dental filler comprising a treated surface, the method comprising treating the surface of the dental filler with a caseinate.
20. The method of claim 19 wherein the caseinate comprises a salt of calcium, phosphate, fluoride, or combinations thereof.

21. The method of claim 19, wherein treating is selected from the group consisting of coating, infiltrating, and combinations thereof.
22. The method of claim 19, wherein treating comprises:
dissolving, dispersing, or suspending the caseinate in a liquid;
combining the liquid with the dental filler; and
removing at least a portion of the liquid to provide the treated surface.
23. The method of claim 22 wherein the liquid is non-aqueous.
24. The method of claim 22 wherein the liquid comprises water.
25. The method of claim 19, wherein the dental filler is porous.
26. The method of claim 25, wherein the porous dental filler is selected from the group consisting of porous particles, porous agglomerates of particles, and combinations thereof.
27. The method of claim 19, wherein the dental filler comprises nanoparticles, agglomerates of nanoparticles, or combinations thereof.
28. The method of claim 19, wherein the dental filler comprises metal oxides, metal fluorides, metal oxyfluorides, or combinations thereof.
29. The method of claim 28, wherein the metal is selected from the group consisting of heavy metals, non-heavy metals, and combinations thereof.
30. The method of claim 19, 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.

31. The method of claim 30, 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.
32. The method of claim 19, wherein the dental filler comprises a glass, an amorphous material, or a crystalline material.
33. The method of claim 19, wherein the dental filler comprises a source of fluoride ions.
34. The method of claim 33, wherein the dental filler comprises a fluoroaluminosilicate glass.
35. The method of claim 19, wherein the treated surface further comprises a silane.
36. The method of claim 19, wherein the treated surface further comprises a source of fluoride ions.
37. The method of claim 19, wherein the treated surface further comprises an antibacterial agent.
38. The method of claim 19, wherein the treated surface further comprises Sr, Mg, Zn, Sn, Ag, or combinations thereof.
39. A dental composition comprising a dental filler according to claim 1.
40. The dental composition of claim 39, wherein the caseinate comprises a salt of calcium, phosphate, fluoride, or combinations thereof.
41. The dental composition of claim 39 further comprising an additional filler.

42. The dental composition of claim 39 further comprising water.
43. The dental composition of claim 39 further comprising a water-dispersible, polymeric film former.
44. The dental composition of claim 39 further comprising a hardenable resin.
45. The dental composition of claim 44, wherein the hardenable resin comprises acid functionality.
46. The dental composition of claim 45, wherein the acid functionality comprises carboxylic acid functionality, phosphoric acid functionality, phosphonic acid functionality, sulfonic acid functionality, or combinations thereof.
47. The dental composition of claim 44 further comprising an initiator system.
48. The dental composition of claim 44, wherein the hardenable resin comprises an ethylenically unsaturated compound.
49. The dental composition of claim 48, 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.
50. The dental composition of claim 39, 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.

51. A method of treating a tooth structure comprising contacting the tooth structure with a dental composition according to claim 39.
52. A method of remineralizing a tooth structure comprising placing a dental composition according to claim 40 in an oral environment.
53. A method of reducing sensitivity of a tooth structure comprising placing a dental composition according to claim 40 in an oral environment.
54. A method of protecting a tooth structure comprising placing a dental composition according to claim 40 in an oral environment.
55. A method of delivering ions to an oral environment comprising:
placing a dental composition according to claim 40 in the oral environment, wherein the ions comprise elements selected from the group consisting of calcium, phosphorus, fluorine, and combinations thereof.
56. 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.
57. A dental composition comprising:
a hardenable resin; and
a caseinate, wherein the caseinate is at least partially dissolved, suspended, or dispersed in the hardenable resin.
58. The dental composition of claim 57, wherein the caseinate comprises a salt of calcium, phosphate, fluoride, or combinations thereof.

59. The dental composition of claim 57, wherein the hardenable resin comprises acid functionality.
60. The dental composition of claim 59, wherein the acid functionality comprises carboxylic acid functionality, phosphoric acid functionality, phosphonic acid functionality, sulfonic acid functionality, or combinations thereof.
61. The dental composition of claim 57, further comprising an initiator system.
62. The dental composition of claim 57 further comprising an additional filler.
63. The dental composition of claim 57, wherein the hardenable resin comprises an ethylenically unsaturated compound.
64. The dental composition of claim 63, 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.
65. The dental composition of claim 57, 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.
66. A method of treating a tooth structure comprising contacting the tooth structure with a dental composition according to claim 57.

67. A method of remineralizing a tooth structure comprising placing a dental composition according to claim 58 in an oral environment.
68. A method of reducing sensitivity of a tooth structure comprising placing a dental composition according to claim 58 in an oral environment.
69. A method of protecting a tooth structure comprising placing a dental composition according to claim 58 in an oral environment.
70. A method of delivering ions to an oral environment comprising:
placing a dental composition according to claim 58 in the oral environment, wherein the ions comprise elements selected from the group consisting of calcium, phosphorus, fluorine, and combinations thereof.
71. A method of preparing a dental article comprising:
combining a caseinate 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.
72. The method of claim 71, wherein the caseinate comprises a salt of calcium, phosphate, fluoride, or combinations thereof.
73. A dental composition comprising:
a water-dispersible, polymeric film former; and
a caseinate, wherein the caseinate is at least partially dissolved, suspended, or dispersed in the film former.
74. The dental composition of claim 73, wherein the caseinate comprises a salt of calcium, phosphate, fluoride, or combinations thereof.

75. A method of treating a tooth structure comprising contacting the tooth structure with a dental composition according to claim 73.
76. A method of remineralizing a tooth structure comprising placing a dental composition according to claim 74 in an oral environment.
77. A method of reducing sensitivity of a tooth structure comprising placing a dental composition according to claim 74 in an oral environment.
78. A method of protecting a tooth structure comprising placing a dental composition according to claim 74 in an oral environment.
79. A method of delivering ions to an oral environment comprising:
placing a dental composition according to claim 74 in the oral environment, wherein the ions comprise elements selected from the group consisting of calcium, phosphorus, fluorine, and combinations thereof.
80. A dental composition comprising:
a dental filler according to claim 1;
a hardenable resin; and
a water-dispersible, polymeric film former.
81. The dental composition of claim 80, wherein the hardenable resin and the water-dispersible, polymeric film former are the same.
82. The dental composition of claim 80, wherein the hardenable resin and the water-dispersible, polymeric film former are different.
83. A dental composition comprising:
a hardenable resin;
a water-dispersible, polymeric film former; and

a caseinate, wherein the caseinate is at least partially dissolved, suspended, or dispersed in one or more of the hardenable resin and the water-dispersible, polymeric film former.

84. The dental composition of claim 83, wherein the hardenable resin and the water-dispersible, polymeric film former are the same.

85. The dental composition of claim 83, wherein the hardenable resin and the water-dispersible, polymeric film former are different.