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(54) Title: PASTE:PASTE GLASS IONOMER CEMENT SYSTEM AND METHODS

(57) Abstract

The present invention provides a multiple part photocurable ionomeric cement system. The first part is an aqueous paste comprising a photocurable ionomer having sufficient pendent ionic groups to undergo a setting reaction in the presence of a reactive filler and water and sufficient pendent polymerizable groups to enable the resulting mixture to be cured by exposure to radiant energy. The second part is an organic paste comprising reactive filler. This system provides ionomeric cements exhibiting excellent strength and opacity properties.

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PASTE:PASTE GLASS IONOMER CEMENT SYSTEM AND METHODS

Field of the Invention

This invention relates to glass ionomer cement systems. More specifically, this invention relates to glass ionomer cement systems provided in a paste:paste format.

Background of the Invention

Glass ionomer cements in general are materials that comprise an ionic polymer component and a reactive glass component, where mixing these two components in an aqueous environment initiates a cement setting reaction. These materials are used in a number of applications in the dental and medical industries where a cement is used on, for example, tooth or bone structure. Conventionally, these materials are provided in two part systems, wherein one of the parts is in a powder form. Typically, the ionic polymer is provided in an aqueous liquid form and the reactive glass is provided as a powder. Considerable effort has been expended in designing systems to mix a powder and a liquid quickly and easily to enable complete reaction of conventional glass ionomer systems.

US Patent No. 4,288,355 to Anderson discloses surgical cement compositions comrising a concentrated non-gelling aqueous solution of a polycarboxylic acid and an aqueous suspension of metal oxide powder which when mixed together form a plastic mass which is formable into the desired shape before it hardens. These cements are formulated using a paste:paste format, but in all cases both pastes are aqueous pastes. This reference fails to disclose use of an organic paste for delivery of the reactive filler.

US Patent No. 4,591,384 to Akahane discloses dental cement compositions comprising a metal oxide and second ingredient capable of reacting with the metal oxide. The composition further comprises a tannic acid derivative that is sparingly soluble in water and a reducing agent that is soluble in water. Various forms of combining these two reactive ingredient are disclosed at column 2, lines 18-27. Included in this recitation is "powder/liquid, powder/paste, paste/paste, paste/liquid and the like," apparently indicating that all forms of delivery are equivalent for the cement system disclosed therein. No examples of paste:paste formulations were described in this reference.

US Patent No. 5,063,257 to Akahane discloses dental glass ionomer cement compositions comprising (a) a polymer of an alpha-beta unsaturated carboxylic acid, (b) a fluoroaluminosilicate glass powder, (c) a polymerizable unsaturated organic compound, (d) a polymerization catalyst, (e) water, (f) a surfactant and (g) a reducing agent. Paste:paste compositions are exemplified having the ionomer in an aqueous paste and the reactive filler in an organic paste. This reference, however, explicitly states at column 2, lines 31-50 that it is preferred that the polymerizable unsaturated organic compound does not undergo reaction with the glass powder.

US Patent No. 4,678,436 to Kondo discloses a color-changable cement composition wherein the composition changes color tone with the change in pH to enable visual observation of the degree of setting of the cement composition. Various forms of the components of this cement are disclosed at column 2, lines 27-30, including "powder-liquid, powder-paste, paste-paste, paste-liquid, liquid-liquid," apparently indicating that all forms of delivery are equivalent

for the cement system disclosed therein. Only powder:liquid delivery of the glass ionomer cements is exemplified.

US Patent No. 5,154,762 to Mitra et. al discloses a Univeral Water-Based Medical and Dental Cement, wherein the cement contains water, acid-reactive filler, water-miscible acidic polymer, an ethylenically-unsaturated moiety, photoinitiator, water-soluble reducing agent and water-soluble oxidizing agent. Two-part paste:paste formulations are broadly disclosed at column 2, lines 58-66, with no suggestion that a glass ionomer cement comprising a photocurable ionomer when provided in a paste:paste format will exhibit superior opacity and strength properties.

Summary of the Invention

The present invention provides a multiple part photocurable ionomeric cement system comprising:

(a) an aqueous paste comprising a photocurable ionomer having sufficient pendent ionic groups to undergo a setting reaction in the presence of a reactive filler and water and sufficient pendent polymerizable groups to enable the resulting mixture to be cured by exposure to radiant energy, and

(b) an organic paste comprising reactive filler.

Detailed Description

Applicants have discovered that paste:paste formulations of glass ionomer cement materials as described herein exhibit properties that are superior to like glass ionomer cement materials when provided in the conventional powder:liquid format. Specifically, glass ionomer systems that contain a polymer that comprises both pendent ionic groups and pendent polymerizable groups surprisingly benefit from this

formulation. Additionally, it has been found that it is essential to provide the reactive filler of the glass ionomer system as an organic paste and not in an aqueous formulation.

The glass ionomer cement system as set forth above provides surprisingly superior strength and opacity properties as compared to a like formulation of photocurable ionomer with reactive filler where the ionomer is provided as a liquid and the reactive filler is provided as a dry powder.

Strength is important for glass ionomer cement systems because they may be subjected to occlusal forces or may have to serve as the foundation for an overlying crown. Strength may be measured as compressive strength and as diametral tensile strength. Surprisingly compositons of the present invention have a compressive strength of a Diametral strength greater than 10% higher than a like system provided in a powder:liquid format.

Unpigmented glass ionomer cement systems preferably have a visual opacity in the range of less than about 0.8, in order to provide a life-like appearance to the restoration of the tooth structure. More preferably, the visual opacity is less than 0.6, and most preferably less than 0.4. It has surprisingly been found that the present paste:paste glass ionomer cement systems provide superior visual opacity to like systems wherein the formulation is provided as a conventional powder:liquid formulation.

For purposes of the present invention, a paste is defined as a material wherein the irelastic modules is less than the elastic modulus of the materal. An organic paste is a paste made from organic liquid components, wherein said organic paste is substantially

free of water. Preferably, the aqueous paste and the organic paste each have a viscosity between about 1×10^2 and 1×10^{11} Cps. More preferably, the aqueous paste and the organic paste each have a viscosity between about 1×10^7 and 1×10^9 Cps. Viscosity is measured using a rheometer at a shear rate between 0.01 and 0.1 sec^{-1} at about 25°C. A preferred test protocol is to utilize a Bohlin CS50 controlled stress rheometer (Metric Group, Inc., Bohlin Instruments Division, Cranbury, NJ) with 20 mm parallel plates and a gap of 2mm. The stress is ramped from 1 Pascal up to a stress sufficient to reach a shear rate of approximately 0.1 sec^{-1}.

The term "photocurable ionomer", as used herein, refers to a polymer having sufficient pendent ionic groups to undergo a setting reaction in the presence of a reactive filler and water, and sufficient pendent polymerizable groups to enable the resulting mixture to be polymerized, i.e., cured upon exposure to radiant energy.

The term "reactive filler", as used herein, refers to a metal oxide or hydroxide, mineral silicate, or ion-leachable glass that is capable of reacting with the ionomer in the presence of water to form a hydrogel.

The term "non-reactive filler", as used herein, refers to filler materials that do not react with the ionomer in the presence of water to form a hydrogel.

The term "ionomer cement system", as used herein, refers to the unmixed, or mixed but unset and uncured, combination of photocurable ionomer, reactive filler, and other optional ingredients, such as water.

The term "working time", as used herein, refers to the time between the beginning of the setting reaction, i.e., when the ionomer and reactive filler are combined

in the presence of water, and the time the setting reaction has proceeded to the point at which it is no longer practical to perform further physical work upon the system, e.g., spatulate it or reform it, for its intended dental or medical purpose.

The term "setting time", as used herein, refers to the time between the beginning of the setting reaction in a restoration, and the time sufficient hardening has occurred to allow subsequent clinical procedures to be performed on the surface of the restoration. Such hardening can occur either in the course of the normal setting reaction and/or by curing a photocurable system.

Photocurable ionomers of the present invention comprise a polymer having sufficient pendent ionic groups to undergo a setting reaction in the presence of a reactive filler and water, and sufficient pendent polymerizable groups to enable the resulting mixture to be cured by exposure to radiant energy.

Preferred photocurable ionomers have the general Formula I:

$$B(X)_m(Y)_n \qquad I$$

wherein

B represents an organic backbone,

each X independently is an ionic group capable of undergoing a setting reaction in the presence of water and a reactive filler,

each Y independently is a photocurable group,

m is a number having an average value of 2 or more, and

n is a number having an average value of 1 or more.

Preferably the backbone B is an oligomeric or polymeric backbone of carbon-carbon bonds, optionally containing non-interfering substituents such as oxygen, nitrogen or sulfur heteroatoms. The term "non-interfering" as used herein refers to substituents or linking groups that do not unduly interfere with either the photocuring reaction of the photocurable ionomer or its dark reaction with the reactive filler.

Preferred X groups are acidic groups, with carboxyl groups being particularly preferred.

Suitable Y groups include, but are not limited to, polymerizable ethylenically unsaturated groups and polymerizable epoxy groups. Ethylenically unsaturated groups are preferred, especially those that can be polymerized by means of a free radical mechanism, examples of which are substituted and unsubstituted acrylates, methacrylates, alkenes and acrylamides. In aqueous systems, polymerizable groups that are polymerized by a cationic mechanism, e.g., polymerizable ethylenically unsaturated groups such as vinyl ether groups and polymerizable epoxy groups, are less preferred since a free radical mechanism is typically easier to employ in such systems than a cationic mechanism.

X and Y groups can be linked to the backbone B directly or by means of any non-interfering organic linking group, such as substituted or unsubstituted alkyl, alkoxyalkyl, aryl, aryloxyalkyl, alkoxyaryl, aralkyl, or alkaryl groups.

Photocurable ionomers of Formula I can be prepared according to a variety of synthetic routes, including, but not limited to, (1) reacting n X groups of a polymer of the formula $B(X)_{m+n}$ with a suitable compound in order to form n pendent Y groups, (2) reacting a polymer of the formula $B(X)_m$ at positions other than the X groups with a suitable compound in order to form

n pendent Y groups, (3) reacting a polymer of the formula $B(Y)_{m+n}$ or $B(Y)_n$, either through Y groups or at other positions, with a suitable compound in order to form m pendent X groups. and (4) copolymerizing appropriate monomers, e.g., a monomer containing one or more pendent X groups and a monomer containing one or more pendent Y groups.

The first synthetic route referred to above is preferred, i.e., the reaction of n X groups of a polymer of the formula $B(X)_{m+n}$ to form n pendent Y groups. Such groups can be reacted by the use of a "coupling compound", i.e., a compound containing both a Y group and a reactive group capable of reacting with the polymer through an X group in order to form a covalent bond between the coupling compound and the X group, thereby linking the Y group to the backbone B in a pendent fashion. Suitable coupling compounds are organic compounds, optionally containing non-interfering substituents and/or non-interfering linking groups between the Y group and the reactive group.

Particularly preferred photocurable ionomers of Formula I are those in which each X is a carboxyl group and each Y is an ethylenically unsaturated group that can be polymerized by a free radical mechanism. Such ionomers are conveniently prepared by reacting a polyalkenoic acid (e.g., a polymer of formula $B(X)_{m+n}$ wherein each X is a carboxyl group) with a coupling compound containing both an ethylenically unsaturated group and a group capable of reacting with a carboxylic acid group. The molecular weight of the resultant photocurable ionomers is preferably between about 250 and about 500,000, and more preferably between about 5,000 and about 100,000. These ionomers are generally water-soluble, but to a lesser extent than the polyalkenoic acids from which they are derived. Hence,

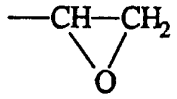
the use of cosolvents, as described more fully below, is preferred in order to enhance the solubility of the ionomers and achieve more concentrated solutions thereof.

Suitable polyalkenoic acids for use in preparing ionomers of this invention include those homopolymers and copolymers of unsaturated mono-, di-, or tricarboxylic acids commonly used to prepare glass ionomer cements. Representative polyalkenoic acids are described, for example, in U.S. Pat. Nos. 3,655,605, 4,016,124, 4,089,830, 4,143,018, 4,342,677, 4,360,605 and 4,376,835.

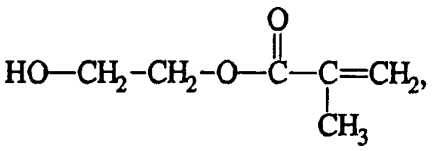
Preferred polyalkenoic acids are those prepared by the homopolymerization and copolymerization of unsaturated aliphatic carboxylic acids, for example acrylic acid, 2-chloroacrylic acid, 3-chloroacrylic acid, 2-bromoacrylic acid, 3-bromoacrylic acid, methacrylic acid, itaconic acid, maleic acid, glutaconic acid, aconitic acid, citraconic acid, mesaconic acid, fumaric acid and tiglic acid. Suitable monomers that can be copolymerized with the unsaturated aliphatic carboxylic acids include unsaturated aliphatic compounds such as acrylamide, acrylonitrile, vinyl chloride, allyl chloride, vinyl acetate, and 2-hydroxyethyl methacrylate. Ter- and higher polymers may be used if desired. Particularly preferred are the homopolymers and copolymers of acrylic acid. The polyalkenoic acid should be surgically acceptable, that is, it should be substantially free from unpolymerized monomers and other undesirable components. Particularly preferred polyalkenoic acids also include homopolymers of polyacrylic acid, and copolymers of acrylic and itaconic acids, acrylic and maleic acids, methyl vinyl ether and maleic anhydride or maleic acid, ethylene and maleic anhydride or maleic acid, and styrene and maleic anhydride or maleic acid.

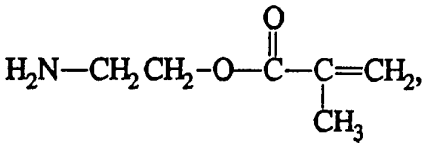
Polymers of formula $B(X)_{m+n}$ can be prepared by copolymerizing an appropriate mixture of monomers and/or comonomers. Preferably, such polymers are prepared by free radical polymerization, e.g., in solution, in an emulsion, or interfacially. Such polymers can be reacted with coupling compounds in the presence of appropriate catalysts.

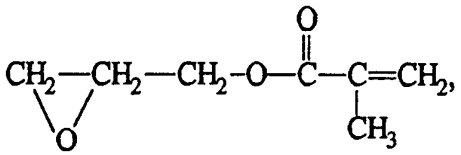
Coupling compounds suitable for use for preparing the preferred ionomers of the present invention include compounds that contain at least one group capable of reacting with X in order to form a covalent bond, as well as at least one polymerizable ethylenically unsaturated group. When X is carboxyl, a number of groups are capable of reacting with X, including both electrophilic and nucleophilic groups. Examples of such groups include the following moieties, and groups containing these moieties: -OH, $-NH_2$, -NCO, -COCl, and

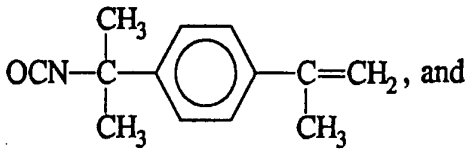


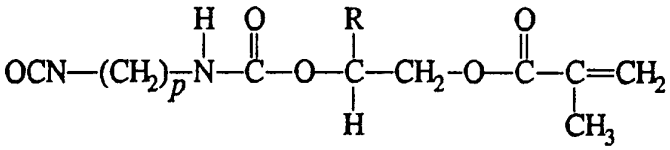
Examples of suitable coupling compounds include, but are not limited to, acryloyl chloride, methacryloyl chloride, vinyl azalactone, allyl isocyanate, 2-hydroxyethylmethacrylate, 2-aminoethylmethacrylate, and 2-isocyanatoethyl methacrylate. Other examples of suitable coupling compounds include those described in U.S. Pat. No. 4,035,321, the disclosure of which is hereby incorporated by reference. Examples of preferred coupling compounds include, but are not limited to, the following methacrylate compounds and their corresponding acrylates.



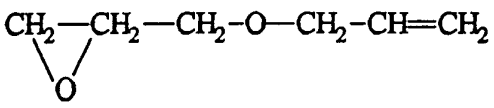




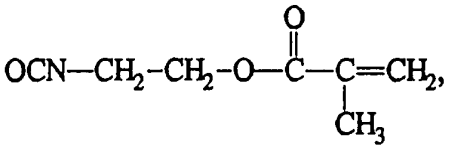


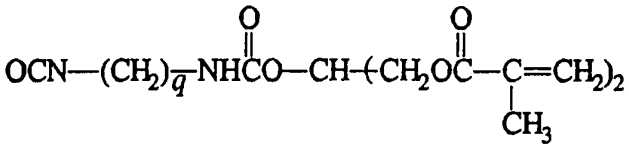


wherein p is 1 to 20 and R is H or lower alkyl (e.g., having 1 to 6 carbon atoms), as well as the following allyl compound

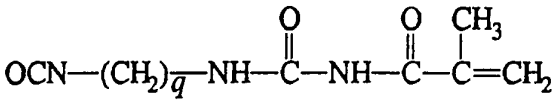


Particularly preferred coupling compounds are the following methacrylate compounds and their corresponding acrylates, wherein R is as defined above.

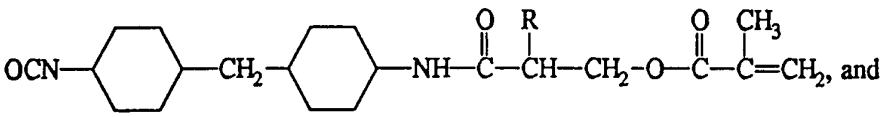


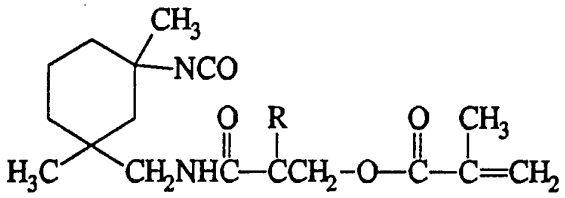


wherein q is 1 to 18.



wherein q is as defined above,





Preferred photocurable ionomers of Formula I are prepared by reacting a polymer of formula $B(X)'_{m+n}$ wherein X is COOH with a coupling compound containing a reactive group of the formula NCO. The resultant ionomers, e.g., those of Formula I above wherein the covalent bond between the X group and the reactive group of the coupling compound is an amide linkage. These inomers provide an optimal combination of such properties as adhesion to dentin, mechanical strength, working time, fluoride release and the like.

Reactive fillers suitable for use in the cement systems of this invention include those that are commonly used with ionomers to form ionomer cements. Examples of suitable reactive fillers include metal oxides such as zinc oxide and magnesium oxide, and ion-leachable glasses, e.g., as described in U.S. Pat. Nos. 3,655,605, 3,814,717, 4,143,018, 4,209,434, 4,360,605 and 4,376,835.

The reactive filler is preferably a finely divided reactive filler. The filler should be sufficiently finely-divided so that it can be conveniently mixed with the other ingredients and used in the mouth. Preferred average particle diameters for the filler are about 0.2 to about 15 micrometers, more preferably about 1 to 10 micrometers, as measured using, for example, a sedimentation analyzer.

Preferred reactive fillers are acid-reactive. Suitable acid-reactive fillers include metal oxides,

metal salts and glasses. Preferred metal oxides include barium oxide, calcium oxide, magnesium oxide and zinc oxide. Preferred metal salts include salts of multivalent cations, for example aluminum acetate, aluminum chloride, calcium chloride, magnesium chloride, zinc chloride, aluminum nitrate, barium nitrate, calcium nitrate, magnesium nitrate, strontium nitrate and calcium fluoroborate. Preferred glasses include borate glasses, phosphate glasses and fluoroaluminosilicate glasses. Fluoroaluminosilicate glasses are particularly preferred. Suitable reactive fillers are also available from a variety of commercial sources familiar to those skilled in the art. For example, suitable fillers can be obtained from a number of commercially available glass ionomer cements, such as "GC Fuji LC" cement and "Kerr XR" ionomer cement. Mixtures of fillers can be used if desired.

If desired, the reactive filler can be subjected to a surface treatment. Suitable surface treatments include acid washing, treatment with phosphates, treatment with chelating agents such as tartaric acid, treatment with a silane or silanol coupling agent. Particularly preferred reactive fillers are silanol treated fluoroaluminosilicate glass fillers, as described in US Patent Application serial number 07/887,619 filed May 22, 1992, entitled METHOD FOR TREATING FLUOROALUMINOSILICATE GLASS," the disclosure of which is expressly incorporated by reference herein.

The amount of reactive filler should be sufficient to provide a cement having desirable mixing and handling properties before cure and good cement performance after cure. Preferably, the reactive filler represents less than about 90%, more preferably about 25% to about 85%, and most preferably about 75%

to about 85% by weight of the total weight of the organic paste components.

Non-reactive fillers may be selected from one or more of any material suitable for incorporation in compositions used for medical applications, such as fillers currently used in dental restorative compositions and the like. The filler is finely divided and preferably has a maximum particle diameter less than about 50 micrometers and an average particle diameter less than about 10 micrometers. The filler can have a unimodal or polymodal (e.g., bimodal) particle size distribution. The filler can be an inorganic material. It can also be a crosslinked organic material that is insoluble in the polymerizable resin, and is optionally filled with inorganic filler. The filler should in any event be non-toxic and suitable for use in the mouth. The filler can be radiopaque, radiolucent or non-radiopaque.

Examples of suitable non-reactive inorganic fillers are naturally-occurring or synthetic materials such as quartz, nitrides (e.g., silicon nitride), glasses derived from, for example Ce, Sb, Sn, Zr, Sr, Ba and Al, colloidal silica, feldspar, borosilicate glass, kaolin, talc, titania, and zinc glass; low Mohs hardness fillers such as those described in U.S. Patent No. 4,695,251; and submicron silica particles (e.g., pyrogenic silicas such as the "Aerosil" Series "OX 50", "130", "150" and "200" silicas sold by Degussa and "Cab-O-Sil M5" silica sold by Cabot Corp.). Examples of suitable non-reactive organic filler particles include filled or unfilled pulverized polycarbonates, polyepoxides, and the like. Preferred non-reactive filler particles are quartz, submicron silica, and non-vitreous microparticles of the type described in U.S. Patent No. 4,503,169. Mixtures of these non-reactive

fillers are also contemplated, as well as combination fillers made from organic and inorganic materials.

Preferably the surface of the filler particles is treated with a coupling agent in order to enhance the bond between the filler and the polymerizable resin. The use of suitable coupling agents include gamma-methacryloxypropyltrimethoxysilane, gamma-mercaptopropyltriethoxysilane, gamma-aminopropyltrimethoxysilane, and the like.

The ionomer cement systems of the invention contain one or more suitable photopolymerization initiators that act as a source of free radicals when activated. Such initiators can be used alone or in combination with one or more accelerators and/or sensitizers.

The photoinitator should be capable of promoting free radical crosslinking of the ethylenically unsaturated moiety on exposure to light of a suitable wavelength and intensity. It also preferably is sufficiently shelf stable and free of undesirable coloration to permit its storage and use under typical dental conditions. Visible light photoinitiators are preferred. The photoinitiator preferably is water soluble or water miscible. Photoinitiators bearing polar groups usually have a sufficient degree of water solubility or water miscibility. The photoinitiator frequently can be used alone, but typically it is used in combination with a suitable donor compound or a suitable accelerator (for example, amines, peroxides, phosphorus compounds, ketones and alpha-diketone compounds).

Preferred visible light-induced initiators include camphorquinone (which typically is combined with a suitable hydrogen donor such as an amine), diaryliodonium simple or metal complex salts,

chromophore-substituted halomethyl-s-triazines and halomethyl oxadiazoles. Particularly preferred visible light-induced photoinitiators include combinations of an alpha-diketone, e.g., camphorquinone, and a diaryliodonium salt, e.g., diphenyliodonium chloride, bromide, iodide or hexafluorophosphate, with or without additional hydrogen donors (such as sodium benzene sulfinate, amines and amine alcohols).

Preferred ultraviolet light-induced polymerization initiators include ketones such as benzyl and benzoin, and acyloins and acyloin ethers. Preferred commercially available ultraviolet light-induced polymerization initiators include 2,2-dimethoxy-2-phenylacetophenone ("IRGACURE 651") and benzoin methyl ether (2-methoxy-2-phenylacetophenone), both from Ciba-Geigy Corp.

The photoinitiator should be present in an amount sufficient to provide the desired rate of photopolymerization. This amount will be dependent in part on the light source, the thickness of the layer to be exposed to radiant energy, and the extinction coefficient of the photoinitiator. Typically, the photoinitiator components will be present at a total weight of about 0.01 to about 5%, more preferably from about 0.1 to about 5%, based on the total weight of the composition.

The ionomer cement system may also incorporate additional modes of initiation of the polymerization reaction to initiate a crosslinking reaction without the need to expose the cement system to visible light. A preferred additional mode for initiation of the polymerization reaction is the incorporation of an oxidizing agent and a reducing agent as a redox catalyst system to enable the dental composition to cure via a redox reaction. Various redox systems and their use in ionomer cements is described in U.S.

Patent No. 5,154,762, the disclosure of which is expressly incorporated herein by reference. A metal complexed ascorbic acid is a preferred reducing agent that provides cure with excellent color stability. This system is more fully described in US Patent application serial No. (attorney docket number 50048USA4A) filed on even date with the present application, the disclosure of which is expressly incorporated herein by reference.

The oxidizing agent should react with or otherwise cooperate with the reducing agent to produce free radicals capable of initiating polymerization of the ethylenically unsaturated moiety. The oxidizing agent and the reducing agent preferably are sufficiently shelf stable and free of undesirable coloration to permit their storage and use under typical dental conditions. The oxidizing agent and the reducing agent should also preferably be sufficiently soluble and present in an amount sufficient to permit an adequate free radical reaction rate. This can be evaluated by combining the ethylenically unsaturated moiety, the oxidizing agent and the reducing agent and observing whether or not a hardened mass is obtained.

Suitable oxidizing agents include persulfates such as sodium, potassium, ammonium and alkyl ammonium persulfates, benzoyl peroxide, hydroperoxides such as cumene hydroperoxide, tert-butyl hydroperoxide, tert-amyl hydroperoxide and 2,5-dihydroperoxy-2,5-dimethylhexane, salts of cobalt (III) and iron (III), hydroxylamine, perboric acid and its salts, salts of a permanganate anion, and combinations thereof. Hydrogen peroxide can also be used, although it may, in some instances, interfere with the photoinitiator, if one is present. The oxidizing agent may optionally be provided in an encapsulated form as described in U.S. Patent No. 5,154,762.

Preferred reducing agents include ascorbic acid, metal complexed ascorbic acid, cobalt (II) chloride, ferrous chloride, ferrous sulfate, hydrazine, hydroxylamine, oxalic acid, thiourea and salts of a dithionite, thiosulfate, benzene sulfinate, or sulfite anion.

Metal complexed ascorbic acid is a particularly preferred reducing agent. The metal complexed ascorbic acid provides a dental composition that exhibits color stability and maintains the catalytic potency of the ascorbic acid. Any metallic ion that can form stable complexes with ascorbic acid can be used. Preferred metals include the transition metals of group IA, IIA, and IIIB. Particularly preferred complexing metals are zirconium and aluminum with aluminum being most preferred. The desired metal complexed ascorbic acid is preferably prepared using a suitable metal alkoxide or metal salt.

An aged dental composition exhibits improved color stability when compared to a similar composition immediately after it has been formulated. This is observed when the ΔE^*_{ab} value of a cured composition after aging for a specific period of time is less than that of a similar composition immediately after it has been formulated.

The color stability of a material is evaluated by measuring in reflection the L^*, a^* and b^* color coordinates of a cured sample after aging and a similar sample immediately after it has been formulated. The color coordinates are obtained by the CIELAB (CIE 1978) color determination methods described in Billmeyer & Saltzman, Principles of Color Technology, 2nd Ed., pp. 62-65 (1981). The ΔL^*, Δa^* and Δb^* values are obtained by subtracting the L^*, a^* and b^* values of a cured sample of the aged material from the L^*, a^* and b^* values of a

cured sample of the same material immediately after it has been formulated.

The ΔE^*_{ab} values are obtained using the CIELAB color difference equation set out in Billmeyer & Saltzman, id. at p. 103. The sample is considered to exhibit color stability if the ΔE^*_{ab} value of the cured sample after aging at 45°C for 5 days is less than the ΔE^*_{ab} value of a similar sample immediately after formulation. More preferably, the sample is considered to exhibit color stability if the ΔE^*_{ab} value of the cured sample after aging at 45°C for 5 days is less than about 5 and most preferably less than about 3.

Having three cure mechanisms in the glass ionomer system (photocure, dark cure through a redox reaction, and ionic cure) facilitates thorough, uniform cure and retention of good clinical properties. Cements utilizing three modes of cure have particular utility in clinical applications where cure of a conventional light-curable composition may be difficult to achieve. Such applications include deep restorations, large crown build-ups, endodontic restorations, luting of metallic crowns or other light-impermeable prosthetic devices to teeth, and other restorative applications in inaccessible areas of the mouth.

For photocurable ionomers that are polymerized by a cationic mechanism, suitable initiators include salts that are capable of generating cations such as the diaryliodonium, triarylsulfonium and aryldiazonium salts.

Optional other ingredients, such as polymerization initiators, modifying agents and cosolvents can be added at any time and in any manner that does not prematurely begin the setting reaction or the photocuring reaction.

Modifying agents can be used in the ionomer cement systems of the present invention in order to provide

prolonged working times. Modifying agents useful in the cement system of the present invention are, for example, alkanolamines, e.g., ethanolamine and triethanolamine, and mono-, di- and tri-sodium hydrogenphosphates. Modifying agents can be incorporated into either or both pastes of the present invention. The modifying agents are preferably used at a concentration between about 0.1 to about 10 percent by weight, based on the weight of the reactive filler, and preferably between about 0.5 to about 5 percent.

Cosolvents useful in the present invention include, but are not limited to, low molecular weight organic solvents. The word "cosolvent", as used herein refers to a material that aids in the dissolution of a photocurable ionomer in water, in order to form a homogeneous aqueous solution of cosolvent and ionomer. Suitable cosolvents include non-copolymerizable organic solvents and copolymerizable low molecular weight hydrophilic alkenyl solvents. The word "copolymerizable" as used herein refers to the ability of the cosolvent to cure compatibly with the ionomers used in the invention. Copolymerizable cosolvents can be added to the ionomer cement systems of this invention for a variety of reasons, for instance, to provide a homogeneous solution of a photocurable ionomer having inherently low aqueous solubility, to shorten the exposure of radiant energy needed to cure the system, or to vary the physical properties, e.g., the flexibility, of the resultant cured ionomer cement. Examples of suitable cosolvents include non-copolymerizable cosolvents such as ethanol, propanol, and glycerol, and copolymerizable cosolvents such as 2-hydroxylethylmethacrylate or 2-hydroxypropyl-methacrylate.

Optionally, the glass ionomer cement may contain stabilizers. The incorporation of stabilizers serves

to further improve the color stability of paste:paste compositions. Suitable stabilizers include oxalic acid, sodium metabisulfite, metaphosphoric acid, sodium bisulfite, sodium thiosulfate, and combinations thereof. Oxalic acid and sodium metabisulfite are preferred stabilizers.

If desired, the cements of the invention can contain adjuvants such as pigments, inhibitors,, accelerators, viscosity modifiers, medicaments and other ingredients that will be apparent to those skilled in the art.

Preferably, the ionomeric cement system is substantially free of surfactant. While not being bound by theory, it is believed that incorporation of surfactant tends to have a deleterious affect on the strength of the resulting hardened cement.

The aqueous pastes of the present invention are formulated by first preparing a solution of the polymerizable ionomer in water, either alone or with the use of adjuvants such as cosolvents described in detail above. A non-reactive filler is then mixed with the ionomer solution in an amount effective to form a paste having the desired viscosity. Optionally, and preferably, the cement system also includes modifying agent and polymerization initiator, thereby providing the ability to achieve a longer working time and a shorter setting time, respectively, when preparing the resultant cement.

An organic paste is prepared by mixing the reactive filler with an organic liquid in an amount sufficient to form a paste having the desired viscosity. Optionally, a non-reactive filler may also be incorporated in the organic paste. Preferably, the organic liquid is selected from monomers that are polymerizable with the photocurable ionomer. Preferred examples of such organic liquids include water miscible

or water soluble acrylates and methacrylates such as 2-hydroxyethyl (meth)acrylate, hydroxymethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, tetrahydrofurfuryl methacrylate, glycerol mono- or di-(meth)acrylate, trimethylol propane tri(meth)acrylate, ethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, urethane (meth)acrylates, acrylamide, methacrylamide, methylene bis-acrylamide or methacrylamide, diacetone acrylamide and methacrylamide, and pentaerithritol (meth)acrylates. Examples of water insoluble or sparingly water soluble liquids include bisphenol A diglycidyl methacrylate ("Bis-GMA), triethylene glycol dimethacrylate ("TEGDMA"). Mixtures of ethylenically unsaturated moieties can be used if desired. A useful list of suitable materials is presented at column 5, line 43 through column 7, line 23 of U.S. Patent No. 5,063,257.

It has further surprisingly been found that addition of submicron silica particles (e.g., pyrogenic silicas such as the "Aerosil" Series "OX 50", "130", "150" and "200" silicas sold by Degussa and "Cab-O-Sil M5" silica sold by Cabot Corp.) to the organic paste substantially improves the handling properties of that paste.

The pastes of the photocurable ionomer cement system can be combined, e.g., blended or mixed, in a variety of manners and amounts in order to form the photocurable ionomer cement of this invention. Mixture by spatulation is an option, but the present formulation lends itself well to novel and advantageous delivery of glass ionomer systems using a multiple barrel syringe delivery system using a static mixing element to assure adequate mixing of the two pastes. Such a system is described in pending U.S. Patent Application serial no. (attorney docket number

50605USA2A) entitled DELIVERY SYSTEM FOR AQUEOUS PASTE DENTAL MATERIALS and U.S. Patent Application serial no. (attorney docket number 50046USA8A) entitled DUAL CHAMBER CARTRIDGE DISPENSING SYSTEM FOR DENTAL MATERIAL filed on even date herewith and assigned to the assignee of the present application, the disclosures of which are expressly incorporated by reference herein.

Sufficient amounts of each component in the cement systems of the present invention should be employed to obtain the desired working time. Preferably such systems will provide a working time of at least about one minute and most preferably greater than two minutes, during which time the systems can be cured by exposure to an appropriate source of radiant energy. For the sake of brevity this discussion will focus on dental applications, and particularly, the curing of such systems in situ, e.g., in the mouth of a patient.

The curing of the ionomer cement system is accomplished by exposure to any source of radiant energy capable of causing the desired extent of polymerization of the photocurable ionomer. Suitable radiant energy sources afford a desired combination of such properties as safety, controllability, suitable intensity, and suitable distribution of incident energy. See generally, "Radiation Curing", Kirk-Othmer Encyclopedia of Chemical Technology 3d Ed., Vol. 19, pp. 607-624 (1982). Preferred radiant energy sources are ultraviolet or visible light sources whose emission spectra correspond closely with the absorption range of the polymerization initiator in the ionomer cement system. For instance, sources emitting ultraviolet light at wavelengths between about 335 and 385 nm, and sources emitting visible light in the blue region at wavelengths between about 420 and 480 nm are preferred for use with the preferred ultraviolet- and visible-light-induced polymerization initiators,

respectively. For polymerizing cement systems in the mouth, visible light radiation such as that provided by standard dental curing lights is particularly preferred.

Upon exposure of an ionomer cement system of the present invention to an appropriate source of radiant energy, the system rapidly begins to cure, e.g., within about 45 seconds, and preferably within about 30 seconds. The restoration generally exhibits the greatest degree of cure near its surface, where the radiant energy is most intense. The surface of the restoration therefore can be cured sufficiently to allow subsequent procedures to be performed on the restoration, while the interior of the restoration is allowed to harden fully by means of the ongoing setting reaction. Thus, if the curing step is omitted, the usual setting reaction will occur, ultimately resulting in the hardening of the material, even in the dark. This phenomenon offers a unique advantage in that a relatively deep restoration can be prepared by rapidly curing the outer surface of the restoration instantly by exposure to radiant energy, allowing the inner portions of the restoration to cure more slowly by the usual setting reaction. As a result, the dentist can continue to carry out further restorative procedures, e.g., layering further ionomer cement on the hardened surface, while the inner portions continue to harden. This can result in a substantial saving of time for the practitioner and patient.

The ionomer cements of this invention can be used in a variety of applications in the dental or medical fields in which a bulk curable material of low shrinkage is desired that will adhere well to the surrounding tooth or bone structure. For instance, these cements can be used as dental restoratives,

liners, bases, cements, sealants and as dental or orthodontic adhesives.

The present invention will be further understood in view of the following examples which are merely illustrative and not meant to limit the scope of the invention. Unless otherwise indicated, all parts and percentages are by weight.

PREPARATORY EXAMPLE 1

Aluminum Ascorbate,
Molar Ratio of Ascorbic Acid:Aluminum = 2:1

Ascorbic acid (10 g, 0.07 moles) was dissolved in 150 ml of methanol. Aluminum butoxide (7 g, 0.035 moles) in 10 ml of isopropanol was added slowly to the ascorbic acid:methanol solution. After addition was complete, the mixture was stirred for 30 minutes with some precipitate observed. Water (10 ml) was then added and the solution stirred for 2 hours. Finally, 100 ml of ethyl acetate was added to precipitate aluminum ascorbate. The aluminum ascorbate was filtered, washed with water and then methanol. The infrared spectrum showed that the carbonyl peak had shifted from 1675 cm^{-1} for unmodified ascorbic acid to 1625 cm^{-1} for the aluminum ascorbate.

PREPARATORY EXAMPLE 2

Zirconium Ascorbate,
Molar Ratio of Ascorbic Acid:Zirconium = 1.7:1

Ascorbic acid (10 g, 0.0567 moles) was dissolved in 200 ml of methanol. Zirconium n-propoxide (70% in n-propanol, 15 ml, 0.0333 moles) was slowly added to the ascorbic acid:methanol solution. After addition was complete, 5 ml of water was added to the resultant

solution to catalyze hydrolysis and condensation of zirconium n-propoxide to zirconium oxide. The solution was stirred for 1 hour before the methanol was distilled off. The precipitate was filtered and washed with water to remove any free ascorbic acid. The white powder was dried in a 45°C oven under vacuum for 24 hours.

PREPARATORY EXAMPLE 3

Zirconium Ascorbate Coated on Zirconium Oxide

Ascorbic acid (40 g) was dissolved in 600 ml of methanol. Zirconium n-propoxide (70% in n-propanol, 60 ml) was slowly added to the ascorbic acid:methanol solution. After addition was complete, the mixture was stirred for 10 minutes with some precipitate observed. Then 60 ml of water was added and the resultant mixture stirred for 2 hours at which time 100 g of zirconium oxide was added and the resultant mixture stirred overnight. The zirconium ascorbate deposited on the zirconium oxide and was isolated by filtration and washed with water.

PREPARATORY EXAMPLE 4

Treated Fluoroaluminosilicate Glass

The ingredients set out below in TABLE I were mixed, melted in an arc furnace at about 1350-1450°C, poured from the furnace in a thin stream and quenched

using chilled rollers to provide an amorphous single-phase fluoroaluminosilicate glass.

TABLE I

Ingredient	Parts
SiO_2	37
AlF_3	23
SrO	20
Al_2O_3	10
$AlPO_4$	7
Na_3AlF_6	6
P_2O_5	4

The glass was ball-milled to provide a pulverized frit with a surface area of 2.5-3.2 m^2/g measured using the Brunauer, Emmet and Teller (BET) method.

A silanol solution was prepared by mixing together 2.0 parts gamma-methacryloxypropyl trimethoxysilane ("A-174", Union Carbide Corp.), 12.6 parts methanol, 12.6 parts water and 0.22 parts acetic acid. The mixture was stirred magnetically for 30 minutes at ambient temperature, added to 50 parts of the glass powder and slurried for 1.5 hours at ambient temperature. The slurry was poured into a plastic-lined tray and dried for 20 hours at 45°C. The silanol treated dried powder was sieved through a 74 micron mesh screen.

PREPARATORY EXAMPLE 5

Treated Zirconia:Silica Filler

25.5 Parts silica sol("LUDOX" LS, E.I. duPont de Nemours & Co.) were acidified by the rapid addition of

0.255 parts concentrated nitric acid. In a separate vessel, 12.9 parts ion-exchanged zirconyl acetate (Magnesium Elecktron Inc.) were diluted with 20 parts deionized water and the resultant solution acidified with 0.255 parts concentrated nitric acid. The silica sol was pumped into the stirred zirconyl acetate solution and mixed for one hour while filtering the stirred mixture through "CUNO" 5 micrometer and 1 micrometer filters (Commercial Intertech Corp.). The stirred, filtered mixture was further filtered though a 1 micrometer "HYTREX" filter (Osmonics, Inc.) followed by a 0.22 micrometer "BALSTRON" filter (Balston Inc.). The filtrate was poured into trays to a depth of about 25 mm and dried at 65°C in a forced air oven for about 24 hours. The resultant dried material was removed from the oven and tumbled through a rotary tube furnace (Harper Furnace Corporation) preheated to 600°C to provide 21 parts of calcined microparticles. The calcined microparticles were comminuted in a tumbling ball mill until all of the microparticles were less than 10 micrometers in particle diameter. 0.3 Part portions of the milled microparticles were placed in ceramic saggers and fired in an electric kiln (Harper Furnace Corporation) in air at 825°C for 1 hour. The fired microparticles were allowed to cool in air. The cooled microparticles were slurried in hydrolyzed A-174 silane, dried in a forced air oven and screened through a 74 micrometer screen. The treated filler particles contained 11.1% silane.

EXAMPLE 1

The ingredients set out below in TABLE II were combined to form a Paste "I", designated Paste Ia.

TABLE II

Ingredient	g
Filler of PREP. EX. 5	65
Copolymer[1]	13
GDMA[2]	9
Bis-GMA	6
Water[3]	7
Zirconium Ascorbate of PREP. EX. 2	0.32

[1] Ethylenically unsaturated acidic copolymer prepared like the precipitated dry polymer of EXAMPLE 11 of U.S. Patent No. 5,130,347

[2] Glycerol dimethacrylate (Rohm Tech, Inc., Malden, MA)

[3] Deionized water

Four Paste Ia formulations were prepared with the addition of 0.65g sodium metabisulfite and/or 0.65g oxalic acid stabilizers as well as without the addition of stabilizer. The resultant Paste Ia formulations were mixed with an equal amount of a Paste "II", designated Paste IIa, prepared by combining the ingredients set out below in TABLE III.

TABLE III

Ingredient	%
Glass of PREP. EX. 4	72.62
Zirconium fluoride	12.40
GDMA	2.15
HEMA[1]	6.91
Bis-GMA	5.23
$K_2S_2O_8$ CAB Encapsulated[2]	0.40
DPI[3]	0.17
CPQ[4]	0.10
BHT[5]	0.02

[1] 2-Hydroxyethyl methacrylate

[2] Microencapsulation in cellulose acetate butyrate prepared according to the procedure of EXAMPLE 9 of U.S. Patent No. 5,154,762

[3] Diphenyliodonium hexafluorophosphate

[4] Camphorquinone

[5] Butylated hydroxytoluene

The set times of the Paste Ia:Paste IIa compositions were measured according to ISO specification 9917. The average set time of all samples prepared immediately after formulation and before aging was 1'30" to 1'40".

The Paste Ia:Paste IIa formulations were formed into 1 mm thick disks by pressing each Paste Ia:Paste IIa mixture into a 1 mm thick x 2 cm diameter steel mold. Each disk was cured with a "VISILUX 2" dental curing light (from 3M) using a 60 second exposure to each side of the sample, and a 1 cm distance between the output end of the light guide and the sample.

Each cured disk was removed from the mold and placed in a 37°C/95% relative humidity chamber for 15 to 30 minutes. Each disk was removed from the chamber and stored in deionized water at room temperature for 15 to 60 minutes. Then each disk was removed from the water, blotted dry with a paper towel and color coordinates immediately measured.

The color coordinates for standard daylight conditions were measured for each disk using a "DINO MATCH SCAN II" color computer (Bausch & Lomb Inc.) with a 25 mm diameter sample port. The L^*, a^* and b^* reflection color coordinates were obtained using the standard white color tile in the reflection sample port.

Each syringe containing the remainder of Paste Ia was aged at 45°C for various time intervals. Each Paste Ia formulation was mixed with an equal amount of Paste IIa, disks were prepared and color coordinates measured as detailed for the samples prepared immediately after formulation.

The ΔL^*, Δa^* and Δb^* values were obtained by subtracting the L^*, a^* and b^* values of a cured sample of the aged material from the L^*, a^* and b^* values of a cured sample of the same material immediately after it has been formulated. The ΔE^*_{ab} values are reported in TABLE IV.

Set out below in TABLE IV are the run no., the stabilizer added to each Paste Ia, the set time of the Paste Ia:Paste IIa compositions at 37°C, the length of time the Paste Ia formulations were aged at 45°C and the ΔE^*_{ab} color value for each Paste Ia:Paste IIa composition.

TABLE IV

Run No.	Stabilizer	Set Time (37°C)	Days (45°C)	ΔE^*_{ab}
1	None	---	3	5.29
		---	9	9.8
2	Oxalic Acid	1'50"	3	3.66
		2'10"	9	13.70
3	$Na_2S_2O_5$	1'40"	3	2.71
		2'10"	9	8.24
4	OA* + $Na_2S_2O_5$	1'50"	3	1.74
		2'	9	1.40

* Oxalic acid

The data in TABLE IV show the improvement in color stability with no significant change in set time of a dental composition containing metal complexed ascorbic acid as well as stabilizers. Even after 9 days at 45°C, the composition of Run no. 4 exhibited excellent color stability with only a slight increase in set time.

EXAMPLE 2

Two Paste I formulations were prepared as in TABLE II except that instead of the 0.32g metal complexed ascorbic acid in Paste Ia, 0.8g of the aluminum ascorbate of PREPARATORY EXAMPLE 1 was incorporated in Paste Ib and 1.6g of the zirconium ascorbate coated on zirconium oxide of PREPARATORY EXAMPLE 3 was incorporated in Paste Ic. Additionally, both Paste Ib

and Paste Ic contained both 0.65g oxalic acid and 0.65g sodium metabisulfite stabilizers.

Paste Ib and Paste Ic were independently mixed with an equal amount of Paste IIa of TABLE III, disks were prepared and color coordinates were measured as described in EXAMPLE 1.

Paste Ib and Paste Ic were then aged at 45°C for 6 and/or 9 days. Aged Paste Ib and Paste Ic were independently mixed with an equal amount of Paste IIa of TABLE III, disks were prepared and color coordinates measured as detailed in EXAMPLE 1.

Set out below in TABLE V are the Paste I composition, the length of time the Paste I was aged at 45°C and the ΔE^*_{ab} color value for each Paste I:Paste IIa composition.

TABLE V

Paste I Composition	Days (45°C)	ΔE^*_{ab}
Ib	6	1.1
Ib	9	2.41
Ic	9	5.75

The data in TABLE V show that the color stability of the paste:paste composition containing aluminum ascorbate (i.e., Paste Ib) was superior to a similar composition containing zirconium ascorbate coated on zirconium oxide filler (i.e., Paste Ic).

EXAMPLE 3

The ingredients set out below in TABLE VI were combined to form Paste Id.

Table VI

Ingredient	g
Filler of PREP. EX. 5	16.25
Copolymer[1]	6.324
GDMA[2]	1.97
Oxalic Acid	0.163
$Na_2S_2O_5$	0.163
Ascorbic Acid (Unmodified)	0.13

[1] Ethylenically unsaturated acidic copolymer prepared like the precipitated dry polymer of EXAMPLE 11 of U.S. Patent No. 5,130,347 containing 26.4% water, 20% HEMA, 6.5% l-tartaric acid and 0.1% BHT

[2] GDMA containing 0.25% CPQ and 0.05% BHT

As a comparison, two additional Paste I formulations, Paste Ie and Paste If, were prepared by combining the ingredients set out in TABLE VI, except that for Paste Ie allantoin ascorbate (prepared according to the procedure of Example 1 of U.S. Patent No. 3,954,989) was substituted for the unmodified ascorbic acid and for Paste If the aluminum ascorbate of PREPARATORY EXAMPLE 1 was substituted for the unmodified ascorbic acid.

The three Paste I formulations were independently hand-loaded into opaque polyethylene syringes and degassed. Each Paste I was independently mixed with an equal amount of Paste IIb which was formed by combining the ingredients set out below in TABLE VII.

TABLE VII

Ingredient	g
Glass of PREP. EX. 4	32
GDMA	8
$K_2S_2O_8$ CAB Encapsulated	0.512
DPI	0.4
CPQ	0.1

Disks of each Paste I:Paste IIb formulation were prepared and color coordinates measured as described in EXAMPLE 1. Then the syringes containing the remainder of Paste Id, Paste Ie and Paste If were placed in a 45°C oven.

On day 5, the Paste I formulations were removed from the oven and independently mixed with an equal amount of Paste IIb. Disks of each composition were prepared and color coordinates measured as detailed in EXAMPLE 1. The remainder of each Paste I formulation was returned to the 45°C oven and the procedure of disk preparation and color coordinate measurement repeated on day 10.

Set out below in TABLE VIII are the Paste I formulations, the number of days the Paste I formulation was aged at 45°C, the L^*, a^* and b^* reflection color coordinates and the ΔE^*_{ab} color value for each Paste I:Paste IIb composition.

TABLE VIII

Paste I Composition	Day	Color Coordinates			ΔE^*_{ab}
		L*	a*	b*	
Paste Id	0	91.69	-3.30	27.56	
	5	92.64	-2.60	23.98	3.77
	10	75.88	-2.72	15.04	20.17
Paste Ie	0	92.28	-3.12	23.61	
	5	92.61	-2.79	24.26	0.81
	10	75.54	-2.82	16.77	18.08
Paste If	0	91.86	-3.80	27.29	
	5	91.84	-3.52	27.93	0.70
	10	91.83	-2.95	31.14	3.94

The data in TABLE VIII show that both the Paste Ie:Paste IIb and the Paste If:Paste IIb compositions exhibited excellent color stability after 5 days aging at 45°C. Already by day 5, the Paste Id:Paste IIb composition had noticeably yellowed. On day 5, it was observed that the Paste Ie composition contained localized areas wherein the composition had gelled, failing to maintain its pre-aged consistency. However, by day 10, only the Paste If:Paste IIb composition continued to exhibit excellent color stability. The Paste If composition contained the aluminum ascorbate, whereas the Paste Ie composition contained the allantoin ascorbate.

EXAMPLE 4

The ingredients set out below in TABLE IX were combined to form Paste Ig.

TABLE IX

Ingredient	%
Filler of PREP. EX. 5	68.1
Copolymer[1]	24
GDMA[2]	6.2
Cumene Hydroperoxide	1.7

[1] Ethylenically unsaturated acidic copolymer prepared like the precipitated dry polymer of EXAMPLE 11 of U.S. Patent No. 5,130,347 containing 26.4% water, 20% HEMA, 6.5% l-tartaric acid and 0.1% BHT

[2] GDMA containing 0.25% CPQ and 0.005% BHT

The ingredients set out below in TABLE X were combined to form Paste IIc.

TABLE X

Ingredient	g
Glass of PREP. EX. 4	77.6
GDMA*	19.8
$Na_2S_2O_5$	1.6
Aluminum Ascorbate of PREPARATORY EXAMPLE 1	1.0

* GDMA containing 1% DPI, 0.25% CPQ and 0.05% BHT

Paste IIc was hand-loaded into an opaque polyethylene syringe and degassed. Paste Ig was mixed with an equal amount of Paste IIc. Disks of Paste Ig:Paste IIc were prepared and color coordinates measured as described in EXAMPLE 1. Then the syringe containing the remainder of Paste IIc was placed in a 45°C oven.

On day 6, the Paste IIc formulation was removed from the oven and mixed with an equal amount of Paste Ig. Disks were prepared and color coordinates measured as detailed in EXAMPLE 1. The remainder of Paste IIc was returned to the 45°C oven and the procedure of disk preparation and color coordinate measurement repeated on day 14.

Set out below in TABLE XI are the Paste Ig:Paste IIc formulation, the number of days the Paste IIc formulation was aged at 45°C, the L^*, a^* and b^* reflection color coordinates and the ΔE^*_{ab} color value for the Paste Ig:Paste IIc composition.

TABLE XI

Paste Ig: Paste IIc	Day	Color Coordinates			ΔE^*_{ab}
		L*	a*	b*	
	0	91.44	-1.38	22.50	
	6	91.36	-6.70	22.49	0.69
	14	92.45	-2.02	22.82	1.24

The data in TABLE XI show the excellent color stability of a paste:paste composition containing the aluminum ascorbate of PREPARATORY EXAMPLE 1 as the reducing agent and cumene hydroperoxide as the oxidizing agent. Even after 14 days at 45°C, the composition maintained excellent color stability.

EXAMPLE 5

Two Paste I compositions, Paste Ih and Paste Ii, were prepared by combining the ingredients set out below in TABLE XII.

TABLE XII

Ingredient	Paste Ih (g)	Paste Ii (g)
Filler of PREP. EX. 5	65.3	65.3
Copolymer*	18.8	10.7
Water	10.2	5.8
GDMA	2.5	9.9
Bis-GMA	1.5	6.6
Oxalic Acid	0.7	0.7
$Na_2S_2O_5$	0.7	0.7
Zirconium Ascorbate of PREP. EX. 2	0.3	0.3

* Ethylenically unsaturated acidic copolymer prepared like the precipitated dry polymer of EXAMPLE 11 of U.S. Patent No. 5,130,347

Eight Paste II compositions, Paste IId-k, were prepared by combining the ingredients set out below in TABLE XIII.

TABLE XIII

Paste	Ingredients (%)					
	Glass[1]	PEG_{200} DMA[2]	Bis-GMA	HEMA	GDMA	PI
IId	76.8	22.8	0	0	0	0.4
IIe	76.8	6.9	10.0	5.9	0	0.4
IIf	76.8	6.9	0	13.6	2.3	0.4
IIg	76.8	18.7	0	0	4.1	0.4
IIh	76.8	8.6	10.0	0	4.2	0.4
IIi	76.8	11.6	7.2	3.0	1.0	0.4
IIj	76.8	14.6	2.2	3.0	3.0	0.4
IIk	76.8	8.6	2.2	8.9	3.1	0.4

[1] Glass of PREP. EX. 4 containing 14.6% ZrF_4 and 0.8% $K_2S_2O_8$

[2] Polyethyleneglycol-200 dimethacrylate (Sartomer, Exton, PA)

[3] Photoinitiator system containing 57.7% DPI, 19.3% CPQ, 19.3% ethyl-4-dimethylaminobenzoate ("EDMAB") and 3.7% BHT

Each Paste I composition was independently hand spatulated for about 10-20 seconds with each Paste II composition in the ratio of 1:1. Each Paste I:Paste II sample was then packed into a 4 mm inside diameter glass tube, capped with silicone rubber plugs and axially compressed at about 0.28 MPa. About 1.5 minutes after the start of mixing, the samples were exposed for 80 seconds to light from two oppositely-disposed visible light curing lamps ("VISILUX 2" curing lamp, from 3M) and then the axial pressure was removed. Each of the samples was allowed to stand for one

hour at ambient pressure, 90%+ relative humidity and 37°C. The samples were cut on a diamond saw to form cylindrical plugs 8 mm long for measurement of compressive strength ("CS") and 2 mm long for measurement of diametral tensile strength ("DTS"). The plugs were stored in distilled water at approximately 37°C for about 24 hours. CS and DTS values were determined for 5 samples of each cement according to ISO specification 7489.

Each Paste I:Paste II composition was formed into disks 20 mm in diameter and 1 mm thick for fluoride release measurement. Both sides of each disk were covered with polyethylene terephthalate film ("PET" film, 0.5 mm thickness, from 3M) and light cured using a 60-80 second exposure to light from a "VISILUX 2" curing lamp placed directly on the PET film.

A fluoride-selective electrode, Orion Model 96-09-00 (from Orion Research Inc., Cambridge, MA) was used to quantify the amount of fluoride ion released from the sample in phosphate buffer. The electrode was calibrated using Fluoride Activity Standards #940907 and #040908, a 100 parts per million ("ppm") and a 10 ppm respectively, fluoride standard fluid (both from Orion Research Inc.).

Each disk was placed in a jar of phosphate buffer having a pH of 6.8-7.0 at 25°C. The phosphate buffer was prepared by mixing 0.7 g KH_2PO_4, 0.71 g Na_2HPO_4 and 1 liter deionized water to provide a 0.01M solution. The fluoride probe was placed in the buffer solution containing the disk on day 0, 5, 16 and 30 and ppm F^- recorded. Micrograms of F^- per gram of the cured disk were then calculated and these values were reported as a function of time of storage in the water. Fluoride release values for 3 samples of each cement were measured and the average recorded.

Set out below in TABLE XIV are the Paste I:Paste II composition, the CS, the DTS and the cumulative fluoride release on day 0, 5, 16 and 30 for each Paste I:Paste II composition compared with a conventional powder:liquid system (Vitrebond™ Light Cure Glass Ionomer Liner/Base from 3M). The powder:liquid mix ratio was 1.4:1.

TABLE XIV

Paste I: Paste II Composition	CS (MPa)	DTS (MPa)	Cumulative F^- Release ($\mu g/g$)			
			Day 0	Day 5	Day 16	Day 30
Ih:IId	179	23	132	804	1055	1408
Ih:IIe	206	26	273	1125	1618	1823
Ih:IIf	154	18	221	963	1388	1593
Ih:IIg	177	23	385	1351	1796	2003
Ih:IIh	199	21	220	1101	1442	1733
Ih:IIi	198	18	223	1397	1948	2348
Ih:IIj	180	9	237	1686	2077	2407
Ih:IIk	172	20	213	1286	1740	2021
Ii:IId	208	30	75	370	588	699
Ii:IIe	231	32	130	282	388	734
Ii:IIf	212	29	147	685	992	1259
Ii:IIg	239	30	209	751	1070	1345
Ii:IIh	198	28	106	291	454	484
Ii:IIi	217	33	116	630	1008	1320
Ii:IIj	217	32	264	1300	1731	2046
Ii:IIk	227	30	159	740	1009	1151
VITREBOND™	96	15	17	470	850	1200

The data in TABLE XIV show that paste:paste formulations according to the present invention exhibit excellent strength properties. These paste:paste

formulations also exhibited excellent fluoride release properties.

EXAMPLE 6

Two Paste II formulations, Paste IIl and Paste IIm, were prepared by combining the ingredients set out below in TABLE XV.

TABLE XV

Ingredient	Paste IIl (%)	Paste IIm (%)
Glass of PREP. EX. 4	76.0	76.0
Bis-GMA	9.7	9.7
$PEG_{200}DMA$	8.9	8.9
GDMA	4.2	4.2
$K_2S_2O_8$	0.8	0.8
Photoiniator	0.4[1]	0.4[2]

[1] The photoinitiator system contained 57.7% DPI, 19.3% CPQ, 19.3% EDMAB and 3.7% BHT

[2] The photoinitiator system contained 57.7% DPI, 19.3% CPQ, and 3.7% BHT

Each Paste II composition was independently hand spatulated for about 10-20 seconds with Paste Ii (from TABLE XIII) in the ratio of 1:1. Samples were prepared and CS and DTS for each Paste I:Paste II composition were measured as described in EXAMPLE 5. Set out below in TABLE XVI are the Paste I:Paste II composition along with the measured CS and DTS for each composition.

TABLE XVI

Paste I:Paste II Composition	CS (MPa)	DTS (MPa)
Ii:IIl	252	40
Ii:IIm	249	34

The data in TABLE XVI show the excellent strength properties provided by paste:paste formulations.

EXAMPLE 7

Two Paste I formulations, Paste Ij and Paste Ik, were prepared by combining the ingredients set out below in TABLE XVII.

TABLE XVII

Ingredient	Paste Ij (%)	Paste Ik (%)
Filler of PREP. EX. 5	66	66
Copolymer*	13.0	11.8
Water	7.9	7.9
GDMA	5	5
HEMA	3.6	3.6
Bis-GMA	3	3
l-Tartaric Acid	1.2	2.4
DPI	0.23	0.23
CPQ	0.07	0.07

* Ethylenically unsaturated acidic copolymer prepared like the precipitated dry polymer of Example 11 of U.S. Patent No. 5,130,347

Paste Ij and Paste Ik were independently hand spatulated for about 10-20 seconds with Paste III (from TABLE XV) in the ratio of 1:1. Samples were prepared and CS and DTS for each Paste I:Paste III composition were measured as described in EXAMPLE 5. Set out below in TABLE XVIII are the Paste I:Paste III composition along with the measured CS and DTS for each composition.

TABLE XVIII

Paste I:Paste II Composition	CS (MPa)	DTS (MPa)
Ij:III	234	30
Ik:III	270	35

The data in TABLE XVIII show that excellent strength properties are obtained in paste:paste formulations.

EXAMPLE 8

Paste Il was prepared by combining the ingredients set out below in TABLE XIX.

TABLE XIX

Ingredient	g
Filler of PREP. EX. 5	16.25
Copolymer[1]	6.324
GDMA[2]	1.97

[1] Ethylenically unsaturated acidic copolymer prepared like the precipitated dry polymer of Example 11 of U.S. Patent No. 5,130,347 containing 26.4% water, 20% HEMA, 6.5% 1-tartaric acid and 0.1% BHT

[2] GDMA containing 1% DPI, 0.25% CPQ, and 0.05% BHT

Paste IIm was prepared by combining the ingredients set out below in TABLE XX.

TABLE XX

Ingredient	g
Glass of PREP. EX. 4	32
GDMA*	8

*GDMA containing 1% DPI, 0.25% CPQ, and 0.05% BHT

A glass ionomer powder was prepared by combining the ingredients set out below in TABLE XXI.

TABLE XXI

Ingredient	g
Glass of PREP. EX. 4	16
Filler of PREP. EX. 5	13

A glass ionomer liquid was prepared by combining the ingredients set out below in TABLE XXII.

TABLE XXII

Ingredient	g
Copolymer[1]	5.4
GDMA[2]	5.6

[1] Ethylenically unsaturated acidic copolymer prepared like the precipitated dry polymer of Example 11 of U.S. Patent No. 5,130,347 containing 26.4% water, 20% HEMA, 6.5% 1-tartaric acid and 0.1% BHT

[2] GDMA containing 0.71% DPI, 0.36% BHT and 0.18% CPQ

Paste Il was hand spatulated for about 10-20 seconds with Paste IIm in the ratio of 1:1. The powder was hand spatulated for about one minute with the liquid in the ratio of 2.5:1. The formulation and the mix ratio of the Paste Il:Paste IIm and the powder:liquid system were prepared to provide final paste:paste and powder:liquid systems that were similar in composition.

Samples were prepared and CS and DTS for the paste :paste and the powder:liquid compositions were measured as described in EXAMPLE 5.

Samples of the paste:paste and the powder:liquid compositions were prepared for visual opacity measurement. 2.54 Millimeter thick by 6 millimeter diameter disks of the cement were cured by exposing the disk to illumination from a "VISILUX 2" dental curing light for 60 seconds on each side at a distance of 6 millimeters. The transmission of light through the thickness of the disk was measured using a MacBeth transmission densitometer Model TD-903 equipped with a visible light filter. The densitometer reading was recorded as the visual opacity value for the disk.

Set out below in TABLE XXIII are the CS, the DTS and the visual opacity values for the paste:paste and the powder:liquid compositions.

TABLE XXIII

Composition	CS (MPa)	DTS (MPa)	Visual Opacity
Paste Il:Paste IIm	284	45	0.33
Powder:Liquid	235	34	0.38

The data in TABLE XXIII show the surprisingly superior properties of a paste:paste glass ionomer system compared to those of a compositionally similar

powder:liquid system. Both the compressive strength and the diametral tensile strength of the paste:paste system are significantly higher than those of the powder:liquid system, while the visual opacity is significantly lower than that of the powder:liquid system.

EXAMPLE 9

Nine liquid formulations were prepared by independently adding the ingredients set out below in TABLE XXIV to a mixture of 0.42 parts HEMA, 1.53 parts water, 1.19 parts GDMA, and 0.022 parts BHT.

TABLE XXIV

Run No.	Ingredients, Parts			
	Copolymer[1]	l-Tartaric acid	DTI[2]	Cumene hydroperoxide
1	1.96	0.27	0	0.24
2	2.10	0.14	0.02	0.16
3	1.96	0.27	0	0.08
4	2.25	0	0	0.08
5	2.25	0	0	0.24
6	1.96	0.27	0.04	0.24
7	2.25	0	0.04	0.08
8	1.96	0.27	0.04	0.08
9	2.25	0	0.04	0.24

[1] Ethylenically unsaturated acidic copolymer prepared like the precipitated dry polymer of EXAMPLE 11 of U.S. Patent No. 5,130,347

[2] Ditolyliodonium triflate

Ten Parts of the filler of PREPARATORY EXAMPLE 5 was independently added to each liquid formulation to provide nine Paste I compositions.

Each Paste I composition was hand-loaded into an opaque polyethylene syringe, degassed and aged at 45°C for 4 days. On day 4, the syringes were removed from the oven and a sample of each aged paste and its corresponding unaged paste were syringed side by side on a white mixing pad. None of the pastes exhibited any visible color change or polymerization.

The ingredients set out below in TABLE XXV were combined to form a Paste II.

TABLE XXV

Ingredients	Parts
Glass of PREP. EX. 4	15.96
GDMA	3.86
EDMAB	0.04
CPQ	0.028
BHT	0.0035
Benzene sulfinic acid sodium salt	0.40

The Paste II composition was hand-loaded into an opaque polyethylene syringe, degassed and aged at 45°C for 7 days. On day 7, the syringe was removed from the oven and a sample of the aged paste and its corresponding unaged paste were syringed side by side on a white mixing pad. The aged paste exhibited no visible color change or polymerization.

EXAMPLE 10

The ingredients set out below in TABLE XXVI were combined to form a Paste I.

TABLE XXVI

Ingredient	Parts
Copolymer*	7.24
HEMA	2.98
Water	3.93
l-Tartaric acid	0.75
GDMA	4.06
BHT	0.03
CPQ	0.004
Cumene hydroperoxide	1.00
Filler of PREP. EX. 5	43.20

* Ethylenically unsaturated acidic copolymer prepared like the precipitated dry polymer of EXAMPLE 11 of U.S. Patent No. 5,130,347

The ingredients set out below in TABLE XXVII were combined to form a Paste II.

TABLE XXVII

Ingredients	Parts
Glass of PREP. EX. 4	25.600
GDMA	6.320
DPI	0.064
CPQ	0.016
BHT	0.003
Benzene sulfinic acid sodium salt	0.480
Sodium thiosulfate	0.640
EDMAB	0.850

Paste I and Paste II were independently hand-loaded into an opaque polyethylene syringe and degassed. Paste I was mixed with an equal amount of Paste II, two disks were prepared and color coordinates were measured on one disk as described in EXAMPLE 1.

The second disk was immediately placed in a container of distilled water and aged at 45°C for 7 days. On day 7, the disk was removed from the water, blotted dry with a paper towel and color coordinates measured as described in EXAMPLE 1.

Set out below in TABLE XXVIII are the L^*, a^*, and b^* reflection color coordinates on day 0 and day 7 and the ΔE^*_{ab} color value of the Paste I:Paste II composition.

TABLE XXVIII

Paste I: Paste II Composition	Day	Color Coordinates			ΔE^*_{ab}
		L*	a*	b*	
	0	92.50	-2.11	22.67	
	7	92.76	-2.74	22.68	0.68

The data in TABLE XXVIII show the excellent color stability on aging exhibited by the Paste I:Paste II composition.

EXAMPLE 11

The ingredients set out below in TABLE XXIX were combined to form a Paste I.

TABLE XXIX

Ingredient	Parts
Copolymer*	7.15
HEMA	1.50
Water	5.52
l-Tartaric acid	0.75
BHT	0.008
GDMA	4.26
Cumene hydroperoxide	0.008
Filler of PREP. EX. 5	35.75

* Ethylenically unsaturated acidic copolymer prepared like the precipitated dry polymer of EXAMPLE 11 of U.S. Patent No. 5,130,347

The ingredients set out below in TABLE XXX were combined to form a Paste II.

TABLE XXX

Ingredient	Parts
Glass of PREP. EX 4	44.0
"OX-50"*	0.2
Sodium benzene sulfinate	1.0
GDMA	10.75
CPQ	0.08
EDMAB	0.10
BHT	0.005
Sodium thiosulfate	0.533

* Pyrogenic silica (Degussa) treated with hydrolyzed A-174 and dried. The treated particles contained about 10.5% silane

Paste I was hand spatulated for about 10-20 seconds with Paste II in the ratio of 1:1. Samples were prepared and CS and DTS were measured as described in EXAMPLE 5. Samples were prepared and visual opacity was measured as described in EXAMPLE 8.

Set out below in TABLE XXXI are the CS, the DTS, and the visual opacity values for the Paste I:Paste II composition.

TABLE XXXI

Paste I:Paste II Composition		
CS (MPa)	DTS (MPa)	Visual Opacity
246	28	0.34

The data in TABLE XXXI show the excellent CS and DTS values of the Paste I:Paste II composition as well as the low visual opacity value.

What is Claimed:

1. A multiple part photocurable ionomeric cement system comprising:

(a) an aqueous paste comprising a photocurable ionomer having sufficient pendent ionic groups to undergo a setting reaction in the presence of a reactive filler and water and sufficient pendent polymerizable groups to enable the resulting mixture to be cured by exposure to radiant energy, and

(b) an organic paste comprising reactive filler.

2. The ionomeric cement system according to claim 1, wherein said aqueous paste and said organic paste each have a viscosity between about 1×10^2 and 1×10^{11} Cps.

3. The ionomeric cement system according to claim 1, wherein said aqueous paste and said organic paste each have a viscosity between about 1×10^5 and 1×10^9 Cps.

4. The ionomeric cement system according to claim 1, wherein the organic paste comprises an organic liquid selected from the group consisting of 2-hydroxyethyl (meth)acrylate, hydroxymethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, tetrahydrofurfuryl methacrylate, glycerol mono- or di-(meth)acrylate, trimethylol propane tri(meth)acrylate, ethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, urethane (meth)acrylates, acrylamide, methacrylamide, methylene bis-acrylamide or methacrylamide, diacetone acrylamide and methacrylamide, and pentaerithritol (meth)acrylates.

5. The ionomeric cement system according to claim 1, wherein the system when cured by intimately mixing the organic paste with the aqueous paste and exposing this mixture to radiant energy has a Diametral Tensile Strength that is greater than ten percent higher than a like cement system provided in a powder:liquid format.

6. The ionomeric cement system according to claim 1, wherein the system when cured by intimately mixing the organic paste with the aqueous paste and exposing this mixture to radiant energy has a Visual Opacity of less than 0.6.

7. The ionomeric cement system according to claim 1, wherein the system when cured by intimately mixing the organic paste with the aqueous paste and exposing this mixture to radiant energy has a Visual Opacity of less than 0.4.

8. The ionomeric cement system according to claim 1, wherein at least one of said polymerizable groups is linked to said ionomer by means of an amide linkage.

9. The ionomeric cement system according to claim 1, wherein said photocurable ionomer has the general Formula I:

$$B(X)_m(Y)_n \qquad I$$

wherein

B represents an organic backbone,

each X independently is an ionic group capable of undergoing a setting reaction in the presence of water and a reactive filler,

each Y independently is a photocurable group,

m is a number having an average value of 2 or more, and

n is a number having an average value of 1 or more.

10. The ionomeric cement system according to claim 9, wherein said X groups are carboxyl groups.

11. The ionomeric cement system according to claim 9, wherein said Y groups are selected from the group consisting of polymerizable ethylenically unsaturated groups and polymerizable epoxy groups.

12. The ionomeric cement system according to claim 9, wherein said X and Y groups are linked to the backbone B by a moiety selected from the group consisting of substituted or unsubstituted alkyl, alkoxyalkyl, aryl, aryloxyalkyl, alkoxyaryl, aralkyl and alkaryl groups.

13. The ionomeric cement system according to claim 1, wherein the aqueous paste comprises a non-reactive filler selected from the group consisting of quartz, colloidal silica, feldspar, strontium glass, barium glass, borosilicate glass, kaolin, talc, titania, zirconia silicate, zinc glass and mixtures thereof.

14. The ionomeric cement system according to claim 1, wherein said system comprises an oxidizing agent selected from the group consisting of sodium persulfate, potassium persulfate, ammonium persulfate, alkyl ammonium persulfate, benzoyl peroxide, cumene hydroperoxide, tert-butyl hydroperoxide, tert-amyl hydroperoxide, the 2,5-dihydroperoxy-2,5-dimethylhexane salt of cobalt (III), the 2,5-dihydroperoxy-2,5-dimethylhexane salt of iron (III), hydroxylamine, perboric acid salt, permanganate anion salt, and combinations thereof.

15. The ionomeric cement system according to claim 1, wherein said system comprises a reducing agent selected from the group consisting of ascorbic acid, metal complexed ascorbic acid, cobalt (II) chloride, ferrous chloride, ferrous sulfate, thiosulfate, hydrazine, hydroxylamine, oxalic acid, thiourea, dithionite salt, sulfite salt, thiosulfate salt, benzene sulfinate salt, and combinations thereof.

16. The ionomeric cement system according to claim 1, wherein said organic paste further comprises submicron silica particles.

17. The ionomeric cement system according to claim 16, wherein said submicron silica particles are pyrogenic silica particles.

18. A method of preparing a cured ionomer cement having high strength and low opacity, said method comprising the steps of

a) intimately mixing

i) an aqueous paste comprising a photocurable ionomer having sufficient pendent ionic groups to undergo a setting reaction in the presence of a reactive filler and water and sufficient pendent polymerizable groups to enable the resulting mixture to be cured by exposure to radiant energy, with

ii) an organic paste comprising reactive filler, and

b) exposing this mixture to radiant energy.

19. A cured ionomer cement prepared by curing by exposure to radiant energy a photocurable cement system, said cement system comprising an intimate mixture of

(a) an aqueous paste comprising a photocurable ionomer having sufficient pendent ionic groups to undergo a setting reaction in the presence of a reactive filler and water and sufficient pendent polymerizable groups to enable the resulting mixture to be cured by exposure to radiant energy, and

(b) an organic paste comprising reactive filler.

20. The ionomeric cement system of claim 1, which system is a component of a kit for treatment of teeth, said kit further comprising one or more materials selected from the group consisting of etchants, restoratives, liners, bases, cements, sealants and adhesives.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A61K

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Cousins-Van Steen, G

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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