ORAL CARE COMPOSITIONS WITH FILM FORMING POLYMERS

INTRODUCTION

[0001] The present invention relates to oral care compositions comprising certain polymers. Embodiments of the present invention include compositions comprising film forming polymers, and methods for whitening teeth using such compositions.

[0002] Many individuals desire a "bright" smile and white teeth, and consider dull and stained teeth cosmetically unattractive. Unfortunately, without preventive or remedial measures, stained teeth are almost inevitable due to the absorbent nature of dental material. Everyday activities such as smoking or other oral use of tobacco products, and eating, chewing or drinking certain foods and beverages (in particular coffee, tea and red wine), cause undesirable staining of surfaces of teeth. Staining can also result from microbial activity, including that associated with dental plaque. The chromogens or color causing substances in these materials become part of the pellicle layer and can permeate the enamel layer. Even with regular brushing and flossing, years of chromogen accumulation can impart noticeable tooth discoloration.

[0003] A tooth is comprised of an inner dentin layer and an outer hard enamel layer that is the protective layer of the tooth. The enamel layer of a tooth is naturally opaque, and white or a slightly off-white color. The enamel layer is composed of hydroxyapatite mineral crystals that create a somewhat porous surface. These hydroxyapatite crystals form microscopic hexagonal rods or prisms that make

up the enamel surface. As a result, the surface of the enamel presents microscopic spaces or pores between the prisms. Without limiting the composition, mechanism, or utility of present invention, it is believed that this porous nature of the enamel is where discoloring substances permeate the enamel and discolor the teeth.

[0004] There are a variety of compositions described in the art for preventing or treating the discoloration of teeth. In particular, to combat staining and brighten or restore the natural enamel color, a variety of products containing bleaching materials are commercially available for professional and consumer use. The most commonly accepted chemicals used in teeth whitening today are peroxides. Peroxides are generally deemed safe from a physiological standpoint, and can be effective to whiten teeth. Such peroxides include hydrogen peroxide, carbamide peroxide, sodium perborate, and sodium percarbonate. When these peroxides are in appropriate contact with teeth they will usually oxidize stains, rendering the teeth whiter.

[0005] Many professional dental treatments include a tooth surface preparation step, such as acid etching, followed by the application of highly concentrated bleaching solutions (e.g., up to 37% hydrogen peroxide) and/or the application of heat or light. (See, e.g., U.S. Patents 5,425,953 and 5,766,574.) These procedures provide rapid results, but are expensive and often require several trips to the dentist. In many treatments, the patient's lips are uncomfortably retracted and the patient is confined to sitting in the dental chair.

[0006] Alternatively, at home bleaching systems can be used. These systems have gained significant popularity in the past decade because of

reduced cost, and increased convenience. Instead of time consuming and frequent trips to the dentist, the tooth whitener is purchased at a consumer retail store and may be used while performing other personal tasks or errands, relaxing or sleeping.

[0007] Current home treatment methods include abrasive toothpastes, toothpastes that produce oxides, whitening gels for use with a dental tray and whitening strips. The effectiveness of such techniques depends on a variety of factors including the type and intensity of the stain, bleaching agent contact time on the teeth, the amount of available bleaching active in the composition, and consumer compliance. Effectiveness is also dependant on the amount of bleaching active in the composition, the ability of the active to be released during use, and the stability of the active in the product. However, the effectiveness of many of these treatments is adversely affected because of deficiencies in one or more factors relating to the composition and consumer compliance.

SUMMARY

[0008] The present invention provides oral care compositions. Embodiments include oral care compositions comprising:

a) an oral care active; and

b) an acrylic film forming polymer.

In various embodiments, such polymers comprise monomeric units selected from the group consisting of acrylic acid, methacrylic acid, acrylates (including methacrylates), and combinations thereof. In one embodiment, the film forming polymer comprises a copolymer of a first monomeric unit selected from the group

consisting of acrylic acid, methacrylic acid, and combinations thereof, with a second monomeric unit selected from the group consisting of acrylates, acrylamides, acetates, and combinations thereof. In various embodiments, the polymer is a terpolymer comprising a combination of the second monomeric units. Preferably, the composition additionally comprises a lower alcohol, preferably ethanol.

[0009] In various embodiments, the present invention provides a whitening composition, wherein the oral care active comprises material, such as a peroxide, that is effective to whiten a tooth surface to which the application is applied. In one embodiment, the present invention provides oral care compositions comprising:

a) a peroxide composite comprising hydrogen peroxide and an N-vinyl heterocyclic polymer; and

b) an acrylic acid polymer comprising a copolymer of a first monomeric unit selected from the group consisting of acrylic acid, methacrylic acid, and combinations thereof, with a second monomeric unit selected from the group consisting of acrylates, acrylamides, acetates, and combinations thereof.

Methods are also provided for whitening a tooth surface, comprising applying a composition comprising a safe and effective amount of a whitening active, such as a peroxide composite, and an acrylic acid polymer.

[0010] It has been discovered that compositions and methods of this invention afford advantages over oral care compositions among those known in the art. Such compositions comprising a whitening active may exhibit one or more of such benefits, including enhanced whitening efficacy, providing a higher available

concentration of bleaching agent, tooth adherence in the presence of saliva without the use of a dental tray and release of the bleaching agent over a period of time. Further uses, benefits and embodiments of the present invention are apparent from the description set forth herein.

DESCRIPTION

[0011] The following definitions and non-limiting guidelines must be considered in reviewing the description of this invention set forth herein. The headings (such as "Introduction" and "Summary,") and sub-headings (such as "Compositions" and "Methods") used herein are intended only for general organization of topics within the disclosure of the invention, and are not intended to limit the disclosure of the invention or any aspect thereof. In particular, subject matter disclosed in the "Introduction" may include aspects of technology within the scope of the invention, and may not constitute a recitation of prior art. Subject matter disclosed in the "Summary" is not an exhaustive or complete disclosure of the entire scope of the invention or any embodiments thereof. Classification or discussion of a material within a section of this specification as having a particular utility (e.g., as being an "active" or a "carrier" ingredient) is made for convenience, and no inference should be drawn that the material must necessarily or solely function in accordance with its classification herein when it is used in any given composition.

[0012] The citation of references herein does not constitute an admission that those references are prior art or have any relevance to the patentability of the invention disclosed herein. Any discussion of the content of references cited in

the Introduction is intended merely to provide a general summary of assertions made by the authors of the references, and does not constitute an admission as to the accuracy of the content of such references. All references cited in the Description section of this specification are hereby incorporated by reference in their entirety, except to the extent (if any) such references are inconsistent with the disclosure of this application.

[0013] The description and specific examples, while indicating embodiments of the invention, are intended for purposes of illustration only and are not intended to limit the scope of the invention. Moreover, recitation of multiple embodiments having stated features is not intended to exclude other embodiments having additional features, or other embodiments incorporating different combinations the stated of features. Specific Examples are provided for illustrative purposes of how to make and use the compositions and methods of this invention and, unless explicitly stated otherwise, are not intended to be a representation that given embodiments of this invention have, or have not, been made or tested.

[0014] As used herein, the words "preferred" and "preferably" refer to embodiments of the invention that afford certain benefits, under certain circumstances. However, other embodiments may also be preferred, under the same or other circumstances. Furthermore, the recitation of one or more preferred embodiments does not imply that other embodiments are not useful, and is not intended to exclude other embodiments from the scope of the invention.

[0015] As used herein, the word 'include," and its variants, is intended to be non-limiting, such that recitation of items in a list is not to the

exclusion of other like items that may also be useful in the materials, compositions, devices, and methods of this invention.

[0016] As referred to herein, all compositional percentages are by weight of the total composition, unless otherwise specified.

Compositions

[0017] The present invention provides oral care compositions and methods for administration or application to, or use with, a human or other animal subject. As referred to herein, an "oral care composition" is any composition that is suitable for administration or application to the oral cavity a human or animal subject for enhancing the health, hygiene or appearance of the subject, preferably providing such benefits as the prevention or treatment of a condition or disorder of the teeth, gums, mucosa or other hard or soft tissue of the oral cavity; the prevention or treatment of a systemic condition or disorder; the provision of sensory, decorative or cosmetic benefits; and combinations thereof. In various preferred embodiments, an oral care composition is not intentionally swallowed, but is rather retained in the oral cavity for a time sufficient to effect the intended utility. Preferably, specific materials and compositions to be used in this invention are pharmaceutically- or cosmetically-acceptable. As used herein, such a "pharmaceutically acceptable" or "cosmetically acceptable" component is one that is suitable for use with humans and/or animals to provide the desired therapeutic, prophylactic, sensory, decorative, or cosmetic benefit without undue adverse side effects (such as toxicity, irritation, and allergic response) commensurate with a reasonable benefit/risk ratio.

[0018] The present invention provides oral care compositions comprising:

a) an oral care active; and

b) an acrylic film forming polymer.

Acrylic Polymer:

[0019] The compositions of the present invention comprise an acrylic film forming polymer. Such polymers comprise monomeric units selected from the group consisting of acrylic acid, methacrylic acid, acrylates, and combinations thereof, and are operable to form a film, preferably when cast on a substrate from a solution. In one embodiment, the compositions of the present invention comprise an acrylic copolymer of a first monomeric unit selected from the group consisting of acrylic acid, methacrylic acid and combinations thereof and a second monomeric unit selected from the group consisting of acrylates, acrylamides, acetates and combinations thereof. Preferred first monomeric units include methacrylic acid or ß-methacrylic acid.

[0020] Second monomeric units include acrylates, acrylamides, acetates and combinations thereof. In one embodiment, the second monomeric unit comprises one or more acrylates. Acrylates include isobutyl acrylate, tert-butyl acrylate, 2-ethylhexyl acrylate, lauryl acrylate, lauryl/tridecyl acrylate, cetyl acrylate, stearyl acrylate, cyclohexyl acrylate, benzyl acrylate, isobornyl acrylate, 2-methoxyethyl acrylate, 2-ethoxyethyl acrylate, 2-ethoxyethoxyethyl acrylate, 2-phenoxyethyl acrylate, tetrahydrofurfuryl acrylate, 2-hydroxyethyl acrylate, 2-

hydroxypropyl acrylate, 4-hydroxybutyl acrylate, dimethylaminoethyl acrylate, and 1,4-butanediol acrylate. Diacrylates include the diacrylates of: 1,4-butanediol, 1,6-hexanediol, tetraethylene glycol, tripropylene glycol, and ethoxylated bisphenol-A. Triacrylate monomers include those of: trimethylol propane, ethoxylated, glyceryl propoxy, and pentaerythritol.

[0021] Acrylates further include methacrylates such as methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate, 2-ethylhexyl methacrylate, lauryl methacrylate, alkyl methacrylate, tridecyl methacrylate, stearyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, isobornyl methacrylate. 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, glycidyl methacrylate, tetrahydrofurfuryl methacrylate, allyl methacrylate, ethylene glycol methacrylate, triethylene glycol methacrylate, tetraethylene glycol methacrylate, 1,3-butyleneglycol methacrylate, 1,6-hexanediol methacrylate, trimethylopropane methacrylate, ethoxyethyl methacrylate and trifluoroethyl methacrylate. Additional preferred second monomeric units include ethyl acrylate, butyl acrylate, N-tertbutyl acrylamide, hydroxyethyl methacrylate, and combinations thereof. A preferred co-polymer is methacrylic acid and ethyl acrylate (Kollicoat ® ,marketed by BASF, Mount Olive, New Jersey, USA).

[0022] Acrylamides includes, but are not limited to, acrylamide, methacrylamide and di(C_1 – C_{30}) alkyl -acrylamides and –methacrylamides such as those of methyl, ethyl, propyl, butyl, pentyl, hexyl and the like. N-substituted acrylamides that are also suitable include N-ethylacrylamide, N-tert-butylacrylamide,

N-tert-octylacrylamide, N-octylacrylamide, N-decylacrylamide, N-dodecylacrylamide and the corresponding N-substituted methacrylamides. Other N-substituted acrylamides include N-hydroxymethyl acrylamide, N-isopropylacrylamide, N-methylacrylamide, N,N'-methylenebisacrylamide, N-isobutoxymethylacrylamide, N,N-dimethylacrylamide and 2-acrylamido-2-methylpropanesulfonic acid.

[0023] Acetates include the salts and esters of acetic acid. A non-limiting example of a salt is the metal salt zinc acetate. Esters include those of with alkyl, aryl, aromatic and vinyl groups and the like. Preferable esters include vinyl acetate. In one embodiment, vinyl acetate, crotonic acid and vinyl neodecanoate are combined to form a preferred polymer for embodiments of this invention (Luviset CAN®, marketed by BASF, Mount Olive, New Jersey, USA).

[0024] In certain embodiments, the polymer is a terpolymer. The terpolymer can comprise a first monomeric unit and two of the same or different second monomeric units. Other preferred terpolymers include the terpolymer of t-butyl acrylate, methacrylic acid and dimethicone copolyol (Luviflex Silk®, marketed by BASF, Mount Olive, New Jersey, USA); and N-tert-butyl acrylamide, ethyl acrylate and acrylic acid (Ultrahold Strong ®, marketed by BASF, Mount Olive, New Jersey, USA).

[0025] In one embodiment, the polymer comprises a terpolymer of acrylates, acrylamides, acetates and combinations thereof. One embodiment comprises ethyl acrylate, t-butyl acrylate and methacrylic acid. Such a polymer is commercially available as Luvimer ®, marketed by BASF, Mount Olive, New Jersey; USA.

[0026] Another preferred polymer additionally comprises a third monomeric unit selected from the group consisting of siloxanes, vinyl esters of C_5 to C_{12} alcohols, and combinations thereof. The siloxane monomer unit includes a silicon-oxygen-silicon bond referred to as a siloxane bond. The monomer can be substituted with hydrocarbon radicals being attached directly via a carbon atom onto the silicon atoms. The most common hydrocarbon radicals are alkyl radicals, especially C_1-C_{10} alkyl radicals. The siloxane is used to create silicones and can be polymerized or polycondensed. Compounds incorporating the siloxane bond include, but are not limited to, hexamethyldisiloxane, octamethyltrisiloxane, linear siloxanes, such as dimethicone and aromatic siloxanes. Siloxane-containing polymers among those useful herein include poly(dimethyl siloxane)-g-polyacrylate polymers, such as 3M Silicone "Plus" Polymers, such as VS80, marketed by 3M Corporation, St. Paul, Minnesota, U.S.A. Vinyl esters suitable for the third monomeric unit include vinyl pentanoate, vinyl hexanoate, vinyl heptanoate, vinyl octanoate, vinyl nonanoate, vinyl decanoate and vinyl dodecanoate.

[0027] Other acrylic polymers useful herein include polyhydroxyethyl methacrylate, sold under the name Poly HEMA, by PolyScience Warrington, Pennsylvania, U.S.A. Other polymers include acrylic acid copolymers such as MG-0560 and MG-0580, marketed by Dow Corning Corporation, Midland, Michigan, U.S.A.

[0028] Other acrylate polymers suitable for use herein are the water swellable polymers and generally formed from acrylic acid, methacrylic acid, methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, and/or other

vinyl monomers. Suitable water swellable polymers include Eudragit® series (E, L, S, RL, RS, and NE), marketed by Rohm Pharma, Piscataway, NJ; USA. A preferred polymer is Eudragit E100. Such polymers are disclosed in U.S. Patent Publication 2003/0235549, Singh et al., published December 25, 2003.

[0029] Preferably, the polymer carrier is alcohol soluble, substantially water insoluble, substantive to the teeth or other surfaces of the oral cavity, and stable to the active material (e.g., peroxide). Preferably such compositions do not exhibit adverse aesthetic effects, such as with respect to taste and mouthfeel (e.g., do not exhibit stickiness to surfaces other than those to which they are applied, or unpleasant texture). Without limiting the composition, method or utility of the present invention, it is believed in various embodiments the polymer have the characteristics of providing a film that is secured against the dental surface. Such embodiments comprise:

a) an active material; and

b) a polymer comprising a hydrophobic moiety and a calcium complexation moiety.

[0030] Preferably, the calcium complexation moiety comprises a monomeric unit selected from the group consisting of acrylic acid, methacrylic acid, and combinations thereof, including first monomeric units as discussed above. Preferably, the hydrophobic moiety comprises a monomeric unit selected from the group consisting of acrylates, acrylamides, acetates, and combinations thereof, including second monomeric units as discussed above. In such an embodiment, the polymer induces additional interaction with the teeth enamel by complexation with

Ca^{2+} components of teeth, such as hydroxyapatite. The complexing provides increased adhesion of the polymer with the teeth and this adhesion affords controlled release of peroxide compound from the composition. The hydrophobic moiety induces resistance of the polymer to removal from the teeth by saliva.

[0031] Oral care compositions of this invention comprise from about 0.2% to about 60% of the polymer. In a most preferred embodiment, the polymer comprises from about 10% to about 30% of the oral care composition.

Active Materials:

[0032] The compositions of the present invention comprise an active material, which is operable for the prevention or treatment of a condition or disorder of hard or soft tissue of the oral cavity, the prevention or treatment of a physiological disorder or condition, or to provide a cosmetic benefit. In various embodiments, the active is a "systemic active" which is operable to treat or prevent a disorder which, in whole or in part, is not a disorder of the oral cavity. In various embodiments, the active is an "oral care active" operable to treat or prevent a disorder or provide a cosmetic benefit within the oral cavity (e.g., to the teeth, gingival or other hard or soft tissue of the oral cavity). Oral care actives among those useful herein include whitening agents, anticaries agents, tartar control agents, antiplaque agents, periodontal actives, abrasives, breath freshening agents, malodor control agents, tooth desensitizers, salivary stimulants, and combinations thereof. It is understood that while general attributes of each of the above categories of actives may differ, there may some common attributes and any given material may serve

multiple purposes within two or more of such categories of actives. Preferably, such actives are selected for compatibility with the peroxide complex, peroxide compound, and with other ingredients of the composition. Actives among those useful herein are disclosed in U.S. Patent Publication 2003/0206874, Doyle et al., published November 6, 2003; U.S. Patent 6,290, 933, Durga et al., issued September 18, 2001; and U.S. Patent 6,685,921, Lawlor, issued February 3, 2004.

[0033] Actives useful herein are optionally present in the compositions of the present invention in safe and effective amounts. A "safe and effective" amount of an active is an amount that is sufficient to have the desired therapeutic or prophylactic effect in the human or lower animal subject to whom the active is administered, without undue adverse side effects (such as toxicity, irritation, or allergic response), commensurate with a reasonable benefit/risk ratio when used in the manner of this invention. The specific safe and effective amount of the active will vary with such factors as the particular condition being treated, the physical condition of the subject, the nature of concurrent therapy (if any), the specific active used, the specific dosage form, the carrier employed, and the desired dosage regimen.

[0034] In various embodiments, the compositions of the present invention comprise a whitening agent. As further discussed below, a "whitening agent" is a material which is effective to effect whitening of a tooth surface to which it is applied. In various embodiments, the compositions of this invention comprise a peroxide whitening agent, comprising a peroxide compound. As referred to herein, a "peroxide compound" is an oxidizing compound comprising a bivalent oxygen-oxygen group. Peroxide compounds include peroxides and hydroperoxides, such as

hydrogen peroxide, peroxides of alkali and alkaline earth metals, organic peroxy compounds, peroxy acids, pharmaceutically-acceptable salts thereof, and mixtures thereof. Peroxides of alkali and alkaline earth metals include lithium peroxide, potassium peroxide, sodium peroxide, magnesium peroxide, calcium peroxide, barium peroxide, and mixtures thereof. Organic peroxy compounds include carbamide peroxide (also known as urea hydrogen peroxide), glyceryl hydrogen peroxide, alkyl hydrogen peroxides, dialkyl peroxides, alkyl peroxy acids, peroxy esters, diacyl peroxides, benzoyl peroxide, and monoperoxyphthalate, and mixtures thereof. Peroxy acids and their salts include organic peroxy acids such as alkyl peroxy acids, and monoperoxyphthalate and mixtures thereof, as well as inorganic peroxy acid salts such as persulfate, dipersulfate, percarbonate, perphosphate, perborate and persilicate salts of alkali and alkaline earth metals such as lithium, potassium, sodium, magnesium, calcium and barium, and mixtures thereof. In various embodiments, the peroxide compound comprises hydrogen peroxide, urea peroxide, sodium percarbonate and mixtures thereof. In one embodiment, the peroxide compound comprises hydrogen peroxide. In one embodiment, the peroxide compound consists essentially of hydrogen peroxide. The peroxide compound comprises from about 0.1% to about 50%, optionally from about 1% to about 40%, optionally from about 10% to about 30% of the oral care composition.

[0035] In one embodiment, the peroxide compound is part of a peroxide composite. In one embodiment, the composite comprises an N-vinyl heterocyclic polymer. Such embodiments of this invention comprise:

a) a peroxide composite comprising hydrogen peroxide and an N-vinyl heterocyclic polymer;

b) an acrylic acid polymer comprising a copolymer of a first monomeric unit selected from the group consisting of acrylic acid, methacrylic acid, and combinations thereof, with a second monomeric unit selected from the group consisting of acrylates, acrylamides, acetates, and combinations thereof; and

c) an orally acceptable non-aqueous carrier.

[0036] In one embodiment, the particulates comprise an N-vinyl heterocyclic polymer which is derived from a N-heterocyclic vinyl monomer, preferably comprising, N-vinyl heterocyclic monomers having from 3 to 7 atoms in a heterocyclic ring, including a carbonyl carbon atom and a nitrogen heteroatom containing a vinyl group. Preferably the ring contains 5 or 6 atoms, comprises heteroatoms such as sulfur or oxygen, and may be substituted or unsubstituted.

[0037] Certain embodiments of such polymers are the polymers of specific N-vinyl heterocyclic monomers such as N-vinyl imides to form poly-N-vinyl polyimides, and N-vinyl lactams to form poly-N-vinyl polylactams, and mixtures thereof. Suitable N-vinyl imides include: N-vinyl malonimide; N-vinyl succinimide; N-vinyl glutarimide; N-vinyl maleimide; N-vinyl β-methylglutarimide; N-vinyl α-amylsuccinimide; and N-vinyl adipimide.

[0038] Suitable N-vinyl lactams include: N-vinyl peperidone; N-vinyl caprolactam; N-vinyl-3-methyl pyrrolidinone or piperidone, or caprolactam; N-vinyl-4-methyl pyrrolidinone, or piperidone or caprolactam; N-vinyl-5-methyl pyrrolidinone or piperidone; N-vinyl-3-ethyl pyrrolidinone; N-vinyl-4,5-dimethyl

pyrrolidinone; N-vinyl-5,5-dimethyl pyrrolidinone; N-vinyl-3,3,5-trimethyl pyrrolidinone; N-vinyl-5-methyl-5-ethyl pyrrolidinone; N-vinyl-3,4,5-trimethyl-3-ethyl pyrrolidinone; N-vinyl-6-methyl-2-piperidone; N-vinyl-6-ethyl-2-piperidone; N-vinyl-3,5-dimethyl-2-piperidone; N-vinyl-4,4-dimethyl-2-piperidone; N-vinyl-7-methyl caprolactam; N-vinyl-7-ethyl caprolactam; N-vinyl-3,5-dimethyl caprolactam; N-vinyl-4,6-dimethyl caprolactam; N-vinyl-3,5,7-trimethyl caprolactam.

[0039] Embodiments containing poly-N-vinyl polylactams, include but are not limited to poly-N-vinyl pyrrolidone, poly-N-vinyl-2-piperidone, poly-N-vinyl-2-caprolactam, poly-N-vinyl-3-methyl-2-caprolacam, poly-N-vinyl-3-methyl-2-piperidone, poly-N-vinyl-4-methyl-2-piperidone, poly-N-vinyl-4-methyl-2-caprolactam, poly-N-vinyl-3-ethyl-2-pyrrolidone, poly-N-vinyl-4,5-dimethyl-2-pyrrolidone and mixtures thereof. Preferably, the polymer is selected from the group consisting of poly-N-vinyl poly-2-pyrrolidone, poly-N-vinyl-poly-2-piperidone, poly-N-vinyl-poly-2-caprolactam and mixtures thereof.

[0040] In a preferred embodiment, the polymer is poly-N-vinyl-poly-2-pyrrolidone. The poly-N-vinyl-poly-2-pyrrolidone is also commonly known as polyvinylpyrrolidone or "PVP". PVP refers to a polymer containing vinylpyrrolidone (also referred to as N-vinylpyrrolidone, N-vinyl-2-pyrrolidione and N-vinyl-2-pyrrolidinone) as a monomeric unit. The monomeric unit consists of a polar imide group, four non-polar methylene groups and a non-polar methane group. The polymers include soluble and insoluble homopolymeric PVPs. Copolymers containing PVP include vinylpyrrolidone/vinyl acetate (also known as Copolyvidone, Copolyvidonum or VP-VAc) and vinylpyrrolidone/dimethylamino-ethylmethacrylate.

[0041] Soluble PVP polymers among those useful herein are known in the art, including Povidone, Polyvidone, Polyvidonum, poly (N-vinyl-2-pyrrolidinone), poly (N-vinylbutyrolactam), poly(1-vinyl-2-pyrrolidone) and poly [1-(2-oxo-1pyrrolidinyl)ethylene]. These PVP polymers are not substantially cross-linked.

[0042] In various embodiments of this invention, an insoluble cross-linked homopolymer is preferred. Such polymers include those common referred to in the art as polyvinylpolypyrrolidone, cross-povidone, PVP and cPVP, and are referred to herein as "cPVP". The homopolymer is prepared by free radical polymerization of the monomer vinylpyrrolidone.

[0043] In one embodiment, the poly-N-vinyl-poly-2-pyrrolidone has a lactam of the pyrrolidone ring that provides the hydrophilic characteristics. Without limiting the composition, mechanism or utility of the invention, it is believed that such groups allow the peroxide compound to bind to the cPVP. The hydrophobic characteristics attributed to the methylene groups in the ring and the linear aliphatic backbone prevent the peroxide complex from reacting with saliva while still maintaining the peroxide available to whiten the teeth. The surface characteristics of the cPVP serve as a barrier to the passage of the peroxide component and prevents the premature distribution of the peroxide component upon application of the oral care composition in the oral cavity. The cPVP linked peroxide is released over a period of time through diffusion, temperature variance, moisture levels and other factors.

[0044] The cPVP is a white or slightly yellow hygroscopic powder. As used herein, "hygroscopic" refers to the property of readily absorbing

moisture. In various embodiments, the polymer has a moisture absorption of from about 10% to about 40% by weight of the peroxide compound.

[0045] cPVP is particularly suitable for trapping a peroxide to form a peroxide polymer composite. Without limiting the composition, mechanism or utility of the present invention, it is believed in various embodiments that the surface characteristics of the cross-linked polymer serves as a barrier to the passage of the peroxide and prevents the premature distribution of the peroxide upon application of the oral care composition to the oral cavity, while maintaining the peroxide available to whiten the teeth.. The cPVP linked peroxide is released over a period of time through diffusion, temperature variance, moisture levels and other factors. This provides a significant advantage over other oral whitening compositions.

[0046] The polymer particulates useful herein are made by well established processes. The poly-N-vinyl polylactams are produced by polymerizing a vinyl lactam in the presence of an alkaline catalyst. (*See* U.S. Patents 2,938,017, Grosser, et al, issued May 24, 1960; 3,277,066, Grosser, et al, issued October 4, 1966 and 3,306,886, Grosser, et al, issued February 28, 1967). Embodiments containing poly-N-vinyl polyimides are produced by heating an N-vinyl imide in the presence of a catalyst. (*See* U.S. Patent No. 3,306,881, Grosser, et al, issued February 28, 1967). In alternative embodiments comprising a co-polymer of the N-vinyl heterocyclic compound is produced by polymerizing N-vinyl heterocyclic and dissimilar vinyl monomers. (*See* U.S. Patent Nos. 2,667,473, Morner, et al, issued January 26, 1954; and 2,947,633, Perry et al, issued August 2, 1960).

[0047] Porous cross-linked polymers among those useful herein include those commercially available as: Luvicross®, Kollidon® CL, Divergan® F, Divergan HM and Divergan RS, marketed by BASF, Mount Olive, New Jersey, USA; and PolyPlasdone®, marketed by ISP, Wayne, New Jersey, USA. It is understood that embodiments of the invention are not limited to a PVP of a specific molecular weight and that any equivalent PVP of acceptable purity, preferably pharmaceutical grade, is within the scope of embodiments of this invention.

[0048] In various embodiments, the peroxide polymer particulates are made by suspending the polymer (preferably cPVP) in a suitable anhydrous organic solvent. An anhydrous solution of the peroxide component is made, preferably utilizing the same organic solvent as the PVP suspension. The peroxide solution is combined with the PVP suspension in an amount corresponding to the desired molar ration of polymer peroxide of the peroxide complex. See, U.S. Patents 5,108,742, Merianos, issued April 28, 1992; and 4,564,514, Druaz, et al, issued January 14, 1986. In one embodiment, the peroxide complex has an equal (1:1) molar ratio of hydrogen peroxide to the polymer.

[0049] In one embodiment, the concentration of the peroxide complex is limited so that the hydrogen component is no more than 6%, so as to maintain a preferred viscosity. In such an embodiment, the combination of the peroxide complex and peroxide compound comprise a total peroxide concentration of greater than 6%, operable to provide more effective bleaching. Furthermore, in alternative embodiments where a peroxy acid serves as the peroxide compound, the

oxidizing strength of the oral care composition is increased due to the leaving qualities of the RCO_2-component of the peroxy acid.

[0050] The peroxide compound comprises from about 0.1% to about 50% of the oral care composition. In a preferred embodiment, the peroxide comprises from about 2% to about 15% of the oral care composition.

[0051] The compositions of the present invention optionally comprise a non-peroxide whitening agent. Whitening agents among those useful herein include non-peroxy compounds, such as chlorine dioxide, chlorites and hypochlorites. Chlorites and hypochlorites include those of alkali and alkaline earth metals such as lithium, potassium, sodium, magnesium, calcium and barium. Non-peroxide whitening agents also include colorants, such as titanium dioxide and hydroxyapatite. One or more whitening agents are optionally present in a tooth-whitening effective total amount, typically about 0.1% to about 90%, for example about 0.5% to about 50% or about 1% to about 20% by weight of the composition.

[0052] The compositions of the present invention optionally comprise an abrasive. In various embodiments, an abrasive is useful for example as a polishing agent. Any orally acceptable abrasive can be used, but type, fineness (particle size) and amount of abrasive should be selected so that tooth enamel is not excessively abraded in normal use of the composition. Suitable abrasives include silica, for example in the form of silica gel, hydrated silica or precipitated silica, alumina, insoluble phosphates, calcium carbonate, resinous abrasives such as urea-formaldehyde condensation products and mixtures thereof. Among insoluble phosphates useful as abrasives are orthophosphates, polymetaphosphates and

pyrophosphates. Illustrative examples are dicalcium orthophosphate dihydrate, calcium pyrophosphate, β-calcium pyrophosphate, tricalcium phosphate, calcium polymetaphosphate and insoluble sodium polymetaphosphate. One or more abrasives are optionally present in an abrasive effective total amount, typically about 5% to about 70%, for example about 10% to about 50% or about 15% to about 30% by weight of the composition. Average particle size of an abrasive, if present, is generally about 0.1 to about 30 μm, for example about 1 to about 20 μm or about 5 to about 15 μm.

[0053] The compositions of the present invention optionally comprise a tartar control (anticalculus) agent. Tartar control agents among those useful herein include phosphates and polyphosphates (for example pyrophosphates), polyaminopropanesulfonic acid (AMPS), polyolefin sulfonates, polyolefin phosphates, diphosphonates such as azacycloalkane-2,2-diphosphonates (e.g., azacycloheptane-2,2-diphosphonic acid), N-methyl azacyclopentane-2,3-diphosphonic acid, ethane-1-hydroxy-1,1-diphosphonic acid (EHDP) and ethane-1-amino-1,1-diphosphonate, phosphonoalkane carboxylic acids and salts of any of these agents, for example their alkali metal and ammonium salts. Useful inorganic phosphate and polyphosphate salts include monobasic, dibasic and tribasic sodium phosphates, sodium tripolyphosphate, tetrapolyphosphate, mono-, di-, tri- and tetrasodium pyrophosphates, sodium trimetaphosphate, sodium hexametaphosphate and mixtures thereof, wherein sodium can optionally be replaced by potassium or ammonium. Other useful anticalculus agents include polycarboxylate polymers and polyvinyl methyl ether/maleic anhydride (PVME/MA) copolymers, such as those

available under the Gantrez™ brand from ISP, Wayne, New Jersey. One or more anticalculus agents are optionally present in an anticalculus effective total amount, typically about 0.01% to about 50%, for example about 0.05% to about 25% or about 0.1% to about 15%.

[0054] The compositions of the present invention optionally comprise a fluoride ion source useful, for example, as an anti-caries agent. Any orally acceptable fluoride ion source can be used, including potassium, sodium and ammonium fluorides and monofluorophosphates, stannous fluoride, indium fluoride and mixtures thereof. In various embodiments, water-soluble fluoride ion sources are used. One or more fluoride ion sources are optionally present in an amount providing a total of about 0.0025% to about 2%, for example about 0.005% to about 1% or about 0.01% to about 0.3%, of fluoride ions.

[0055] The compositions of the present invention optionally comprise a stannous ion source useful, for example, as a periodontal active, tartar control agent, anticaries agent or tooth desensitizer. Any orally acceptable stannous ion source can be used, including stannous fluoride, other stannous halides such as stannous chloride dihydrate, organic stannous carboxylate salts such as stannous formate, acetate, gluconate, lactate, tartrate, oxalate, malonate and citrate, stannous ethylene glyoxide and the like. One or more stannous ion sources are optionally present in a total amount of from about 0.01% to about 10%, optionally from about 0.1% to about 7% or from about 1% to about 5%.

[0056] The compositions of the present invention optionally comprise an antimicrobial (e.g., antibacterial) agent. Any orally acceptable

antimicrobial agent can be used, including Triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol); 8-hydroxyquinoline and salts thereof; zinc and stannous ion sources such as zinc citrate, zinc sulphate, zinc glycinate, sodium zinc citrate and stannous pyrophosphate; copper (II) compounds such as copper (II) chloride, fluoride, sulfate and hydroxide; phthalic acid and salts thereof such as magnesium monopotassium phthalate; sanguinarine; quaternary ammonium compounds, such as alkylpyridinium chlorides (e.g., cetylpyridinium chloride (CPC), combinations of CPC with zinc and/or enzymes, tetradecylpyridinium chloride, and N-tetradecyl-4-ethylpyridinium chloride,); bisguanides, such as chlorhexidine digluconate, hexetidine, octenidine, alexidine; halogenated bisphenolic compounds, such as 2,2' methylenebis-(4-chloro-6-bromophenol); benzalkonium chloride; salicylanilide, domiphen bromide; iodine; sulfonamides; bisbiguanides; phenolics; piperidino derivatives such as delmopinol and octapinol; magnolia extract; grapeseed extract; thymol; eugenol; menthol; geraniol; carvacrol; citral; eucalyptol; catechol; 4-allylcatechol; hexyl resorcinol; methyl salicylate; antibiotics such as augmentin, amoxicillin, tetracycline, doxycycline, minocycline, metronidazole, neomycin, kanamycin and clindamycin; and mixtures thereof. A further illustrative list of useful antibacterial agents is provided in U.S. Patent 5,776,435, Gaffar, et al., issued July, 7, 1998.

[0057] The compositions of the present invention optionally comprise an antioxidant. Any orally acceptable antioxidant can be used, including butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), vitamin A,

carotenoids, vitamin E, flavonoids, polyphenols, ascorbic acid, herbal antioxidants, chlorophyll, melatonin, and mixtures thereof.

[0058] The compositions of the present invention optionally comprise a saliva stimulating agent, useful for example in amelioration of dry mouth. Any orally acceptable saliva stimulating agent can be used, including without limitation food acids such as citric, lactic, malic, succinic, ascorbic, adipic, fumaric, and tartaric acids, and mixtures thereof. One or more saliva stimulating agents are optionally present in a saliva stimulating effective total amount.

[0059] The compositions of the present invention optionally comprise a breath freshening agent. Any orally acceptable breath freshening agent can be used, including without limitation zinc salts such as zinc gluconate, zinc citrate and zinc chlorite, α-ionone and mixtures thereof. One or more breath freshening agents are optionally present in a breath freshening effective total amount.

[0060] The compositions of the present invention optionally comprise an antiplaque (e.g., plaque disrupting) agent. Any orally acceptable antiplaque agent can be used, including without limitation stannous, copper, magnesium and strontium salts, dimethicone copolyols such as cetyl dimethicone copolyol, papain, glucoamylase, glucose oxidase, urea, calcium lactate, calcium glycerophosphate, strontium polyacrylates and mixtures thereof.

[0061] The compositions of the present invention optionally comprise an anti-inflammatory agent. Any orally acceptable anti-inflammatory agent can be used, including steroidal agents such as flucinolone and hydrocortisone, and nonsteroidal agents (NSAIDs) such as ketorolac, flurbiprofen, ibuprofen, naproxen,

indomethacin, diclofenac, etodolac, indomethacin, sulindac, tolmetin, ketoprofen, fenoprofen, piroxicam, nabumetone, aspirin, diflunisal, meclofenamate, mefenamic acid, oxyphenbutazone, phenylbutazone, and mixtures thereof.

[0062] The compositions of the present invention optionally comprise an H_2 antagonist. H_2 antagonists useful herein include cimetidine, etintidine, ranitidine, ICIA-5165, tiotidine, ORF-17578, lupititidine, donetidine, famotidine, roxatidine, pifatidine, lamtidine, BL-6548, BMY-25271, zaltidine, nizatidine, mifentidine, BMY-52368, SKF-94482, BL-6341A, ICI-162846, ramixotidine, Wy-45727, SR-58042, BMY-25405, loxtidine, DA-4634, bisfentidine, sufotidine, ebrotidine, HE-30-256, D-16637, FRG-8813, FRG-8701, impromidine, L-643728, HB-408.4, and mixtures thereof.

[0063] The compositions of the present invention optionally comprise a desensitizing agent. Desensitizing agents useful herein include potassium citrate, potassium chloride, potassium tartrate, potassium bicarbonate, potassium oxalate, potassium nitrate, strontium salts, and mixtures thereof. Alternatively or in addition a local or systemic analgesic such as aspirin, codeine, acetaminophen, sodium salicylate or triethanolamine salicylate can be used.

[0064] The compositions of the present invention optionally comprise a nutrient. Suitable nutrients include vitamins, minerals, amino acids, and mixtures thereof. Vitamins include Vitamins C and D, thiamine, riboflavin, calcium pantothenate, niacin, folic acid, nicotinamide, pyridoxine, cyanocobalamin, para-aminobenzoic acid, bioflavonoids, and mixtures thereof. Nutritional supplements include amino acids (such as L-tryptophane, L-lysine, methionine, threonine,

levocarnitine and L-carnitine), lipotropics (such as choline, inositol, betaine, and linoleic acid), fish oil (including components thereof such as omega-3 (N-3) polyunsaturated fatty acids, eicosapentaenoic acid and docosahexaenoic acid), coenzyme Q10, and mixtures thereof.

[0065] The compositions of the present invention optionally comprise proteins. Suitable proteins include milk proteins and enzymes such as peroxide-producing enzymes, amylase, plaque–disrupting agents such as papain, glucoamylase, glucose oxidase, and "next generation" enzymes."

Orally Acceptable Carrier:

[0066] The present invention provides compositions comprising an orally acceptable carrier. As used herein, an "orally acceptable carrier" refers to a material or combination of materials that are safe for use in the compositions of the present invention, commensurate with a reasonable benefit/risk ratio, with which the peroxide complex may be associated while retaining significant efficacy. Preferably, the carrier does not substantially reduce the efficacy of the active material. Selection of specific carrier components is dependant on the desired product form, including dentifrices, rinses, gels, and paints. In various embodiments, the carrier is operable to sufficiently adhere the active material against surfaces within the oral cavity to which the composition is administered, without concomitant use of a dental tray, mouthpiece, tape, or similar appliance. In various embodiments, the carrier is operable for use with a tape, tray, mouthpiece or similar appliance.

[0067] In various embodiments, the compositions of the present invention comprise no carrier materials. (It is understood, without limiting the composition, function or utility of the present invention that the acrylic acid polymer may function as a carrier in various embodiments.) In other embodiments, the compositions additionally comprise one or more carrier materials. Such carrier materials among those useful herein include adhesion agents, viscosity modifiers, diluents, surfactants, foam modulators, peroxide activators, peroxide stability agents, abrasives, pH modifying agents, humectants, mouth feel agents, sweeteners, flavorants, colorants, and combinations thereof. It is understood that while general attributes of each of the above categories of materials may differ, there may be some common attributes and any given material may serve multiple purposes within two or more of such categories of materials. Preferably, such carrier materials are selected for compatibility with the peroxide complex and with other ingredients of the composition.

[0068] Preferably, the composition comprises a lower (i.e., C_2 – C_5) alcohol, preferably in which the acrylic acid polymer is dissolved. A preferred lower alcohol is ethanol. In one embodiment, the composition comprises an alcohol solution of the acrylic acid polymer, comprising from about 50% to about 60% alcohol, by volume. As discussed above, preferably the acrylic acid polymer is substantive to, and forms a film on, teeth. In one embodiment, such adherence is increased using rheology modifiers that control and maintain the viscosity of the composition at around 10,000 to about 700,000 cps, preferably below about 400,000

cps, and most preferably around 200,000 cps. Suitable rheology modifiers include cPVP, petrolatum, and silicone.

[0069] In various embodiments, the carrier comprises an adhesion agent. As referred to herein, an adhesion agent is a material or combination of materials that enhance the retention of the peroxide complex on the oral cavity surface onto which the composition is applied. Such adhesion agents include adhesives, film forming materials, viscosity enhancers and combinations thereof. Such materials include hydrophilic organic polymers, hydrophobic organic polymers, silicone gums, silicas, and combinations thereof. Adhesion agents are preferably present at a level of from about 0.01% to about 75%, optionally from about 1% to about 40%.

[0070] Hydrophilic organic polymers useful herein include polyethylene glycols, nonionic polymers of ethylene oxide, block copolymers of ethylene oxide and propylene oxide, carboxymethylene polymers, polyvinyl pyrrolidone (PVP) and mixtures thereof. Nonaqueous hydrophilic polymers useful in the practice of the present invention preferably provide a viscosity for the composition in the range between about 10,000 cps to 600,000 cps.

[0071] Hydrophilic polymers also include polymers of polyethylene glycols and ethylene oxide having the general formula:

$$HOCH_2(CH_2OCH_2)_nOH$$

wherein n represents the average number of oxyethylene groups. Polyethylene glycols available from Dow Chemical (Midland, Michigan, U.S.A.) are designated by number such as 200, 300, 400, 600, 2000 which represents the approximate average

molecular weight of the polymer. Polyethylene glycols 200, 300, 400 and 600 are clear viscous liquids at room temperature, and are preferred for use in the practice of the present invention.

[0072] Another hydrophilic polymer useful herein is comprised of a water soluble, nonionic block copolymer of ethylene oxide and propylene oxide of the formula: $HO(C_2H_4O)_a(C_3H_6O)_b(C_2H_4O)_cH$. The block copolymer is preferably chosen (with respect to a, b and c) such that the ethylene oxide constituent comprises from about 65 to about 75% by weight, of said copolymer molecule and the copolymer has an average molecular weight of from about 2,000 to about 15,000, with the copolymer being present in oral care composition.

[0073] A block copolymer useful herein is Pluraflo® L1220, marketed by BASF, Mount Olive, New Jersey, U.S.A., which has an average molecular weight of about 9,800. The hydrophilic poly(ethylene oxide) block averages about 65% by weight of the polymer.

[0074] Organic polymers useful as adhesion enhancing agents include hydrophilic polymers such as carbomers such as carboxymethylene polymers such as acrylic acid polymers, and acrylic acid copolymers. Carboxypolymethylene is a slightly acidic vinyl polymer with active carboxyl groups. A carboxypolymethylene is Carbopol® 974 marketed by Noveon, Inc., Cleveland, Ohio, U.S.A..

[0075] Hydrophobic organic materials useful as adhesion enhancing agents in the practice of the present invention include hydrophobic materials such as waxes such as bees wax, mineral oil, mineral oil and polyethylene

blends (e.g., Plastigel®, marketed by Lyne Laboratories, Brockton, Massachusetts, USA.) petrolatum, white petrolatum, liquid paraffin, butane/ethylene/styrene hydrogenated copolymer) blends (e.g., Versagel®, marketed by Penreco, Houston, Texas, U.S.A.), acrylate and vinyl acetate polymers and copolymers, polyethylene waxes, silicone polymers as discussed further herein and polyvinyl pyrrolidone/vinyl acetate copolymers. In embodiments of the present invention containing a hydrophobic polymer, present in ratios of about 1 to about 85% weight of the composition.

[0076] Silicone polymers useful herein include, but are not limited to, silicone adhesives, silicone elastomers, silicone fluids, silicone resins, silicone gums and mixtures thereof. In one embodiment, the carrier comprises a pressure sensitive adhesive (PSA) composition, including those that are well known in the art. Generally, silicone based PSA's are produced by condensing a silicone resin and an organosiloxane such as a polydiorganosiloxane. Suitable silicone polymers include the copolymer product of mixing a silanol terminated polydiorganosiloxane such as polydimethyl siloxane with a silanol-containing silicone resin whereby the silanol groups of the polydiorganosiloxane undergo a condensation reaction with the silanol groups of the silicone resin so that the polydiorganosiloxane is lightly cross-linked by the silicone resin (that is, the polydiorganosiloxane chains are bonded together through the resin molecules to give chain branching and entanglement and/or a small amount of network character) to form the silicone pressure sensitive adhesive. A catalyst, for example an alkaline material such as ammonia, ammonium hydroxide or ammonium carbonate can be mixed with the silanol-terminated polydiorganosiloxane

and the silicone resin to promote this cross-linking reaction. Copolymerizing the silicone resin with the silanol terminated polydiorganosiloxane affords a self adhering property and cohesive soft elastomer matrix. Modifying the silicone resin to polydiorganosiloxane ratio of the pressure sensitive adhesive will modify the tackiness of the oral care composition. For example PSAs are available from the Dow-Corning Corporation, Midland, Michigan, U.S.A., under the brand name BIO-PSA. A preferred adhesion agent is Dow Corning Silicone Adhesive 8-7016 marketed by Dow-Corning Corporation. The silicone based pressure sensitive adhesive is present in the liquid whitening compositions of the present invention at a concentration of about 0.5% to about 99%, optionally from about 5% to about 60%, optionally from about 10% to about 40%.

[0077] Silicone gums useful herein include high molecular weight polydiorganosiloxanes having a viscosity at 25°C. of from about 500,000 cS up to about 50,000,000 cS. Such silicone gums include those polydiorganosiloxanes with an average molecular weight of greater than 500,000. The polysiloxane gums for use herein can be linear or cyclic, and branched or unbranched. Substituents may have any structure as long as the resulting polysiloxanes are hydrophobic, are not irritating, toxic or otherwise harmful when applied to the oral cavity, and are compatible with the other components of the composition. Specific examples of siloxane gums include polydimethylsiloxane, methylvinylsiloxane, copolymer, poly(dimethylsiloxane, diphenyl, methyvinylsiloxane) copolymer and mixtures thereof. Silicone gums include those commercially available, such as SE30, marketed by General Electric.

[0078] Polysiloxane fluids useful herein include those with a viscosity, at 25° C., of from about 1 cStk to about 1000 cS, preferably from about 2 cS to about 500 cS, and optionally from about 5 cS to about 400 cS. Polysiloxane fluids for use herein can be linear or cyclic, and can be substituted with a wide variety of substituents (including as described above). Preferred substituents include methyl, ehtyl and phenyl substituents. Suitable polysiloxane fluids include linear polysiloxane polymers such as dimethicone and other low viscosity analogues of the polysiloxane materials, preferably having a viscosity at 25°C of 200 cS or less and cyclomethicone, and other cyclic siloxanes having for example a viscosity at 25°C of 200 cS or less. Commercial examples of materials that are suitable for use herein include DC200 series fluids marketed by Dow-Corning Corporation and the AK Fluid series marketed by Wacker-Chemie GmbH, München, Germany.

[0079] Adhesion agents also include inorganic materials. Such inorganic materials include silicon polymers such as amorphous silica compounds which function as thickening agents (e.g., Cab-o-sil® fumed silica manufactured by Cabot Corporation, Boston, Massachusetts, U.S.A.; and Sylox 15 also known as Sylodent 15, marketed by Davison Chemical Division of W.R. Grace & Co., Columbia, Maryland, U.S.A.).

[0080] Thickening agents among those useful herein include carboxyvinyl polymers, carrageenans (also known as Irish moss and more particularly iota-carrageenan), cellulosic polymers such as hydroxyethylcellulose, carboxymethylcellulose (carmellose) and salts thereof (e.g., carmellose sodium), natural gums such as karaya, xanthan, gum arabic and tragacanth, colloidal

magnesium aluminum silicate, colloidal silica and mixtures thereof. One or more thickening agents are optionally present in a total amount of about 0.01% to about 15%, for example about 0.1% to about 10% or about 0.2% to about 5% by weight of the composition.

[0081] Viscosity modifiers among those useful herein include mineral oil, petrolatum, clays and organomodified clays, silica and mixtures thereof. In various embodiments, such viscosity modifiers are operable to inhibit settling or separation of ingredients or to promote redispersibility upon agitation of a liquid composition. One or more viscosity modifiers are optionally present in a total amount of about 0.01% to about 10%, for example about 0.1% to about 5% by weight of the composition.

[0082] Diluents among those useful herein include materials or combinations of materials that are operable to solubilize and/or suspend other components of the composition. In various embodiments, diluents are operable to adjust the viscosity of the composition, optionally in conjunction with viscosity modifiers (as discussed herein) and other components of the composition. The composition is preferably non-aqueous, i.e., does not contain appreciable amounts of chemically-unbound water. In one embodiment, the composition comprises less than about 5% water. Diluents include glycerin and lower alcohols, e.g., ethanol. Diluents are optionally present in the nonaqueous liquid whitening compositions of the present invention in amounts of about 0.1%to about 98%, optionally in various embodiments from about 0.5% to about 70%, from about 0.5% to about 50%, from about 0.5% to about 35%.

[0083] Surfactants among those useful herein include anionic, nonionic, and amphoteric surfactants. Surfactants may be used, for example, to provide enhanced stability of the formulation, to help in cleaning the oral cavity surfaces through detergency, and to provide foam upon agitation, e.g., during brushing with a dentifrice composition of the invention. Suitable anionic surfactants include water-soluble salts of C_{8-20} alkyl sulfates, sulfonated monoglycerides of C_{8-20} fatty acids, sarcosinates, taurates and mixtures thereof. Illustrative examples of these and other surfactants are sodium lauryl sulfate, sodium coconut monoglyceride sulfonate, sodium lauryl sarcosinate, sodium lauryl isoethionate, sodium laureth carboxylate, sodium dodecyl benzenesulfonate, and mixtures thereof. Suitable nonionic surfactants include poloxamers, polyoxyethylene sorbitan esters, fatty alcohol ethoxylates, alkylphenol ethoxylates, tertiary amine oxides, tertiary phosphine oxides, dialkyl sulfoxides and mixtures thereof. Suitable amphoteric surfactants include derivatives of C_{8-20} aliphatic secondary and tertiary amines having an anionic group such as carboxylate, sulfate, sulfonate, phosphate or phosphonate. A suitable example is cocoamidopropyl betaine. One or more surfactants are optionally present in a total amount of about 0.01% to about 10%, for example about 0.05% to about 5% or about 0.1% to about 2%. Preferably, the surfactant is nonionic and compatible with peroxide compounds such as polyethylene oxide. Nonionic surfactants are present in embodiments of this invention at levels of from about 0.01% to about 1%.

[0084] Foam modulators useful herein include materials operable to increase amount, thickness or stability of foam generated by the composition (e.g., dentifrice compositions) upon agitation. Any orally acceptable foam modulator can

be used, including polyethylene glycols (PEGs), also known as polyoxyethylenes. High molecular weight PEGs are suitable, including those having an average molecular weight of about 200,000 to about 7,000,000, for example about 500,000 to about 5,000,000 or about 1,000,000 to about 2,500,000. One or more PEGs are optionally present in a total amount of about 0.1% to about 10%, for example about 0.2% to about 5% or about 0.25% to about 2%.

[0085] Humectants useful herein include polyhydric alcohols such as glycerin, sorbitol, xylitol or low molecular weight PEGs. In various embodiments, humectants are operable to prevent hardening of paste or gel compositions upon exposure to air. In various embodiments humectants also function as sweeteners. One or more humectants are optionally present in a total amount of about 1% to about 50%, for example about 2% to about 25% or about 5% to about 15%.

[0086] Peroxide activators such as sodium bicarbonate, sodium carbonate, manganese gluconate are optionally incorporated in the compositions of the present invention that comprise a peroxide. The activator is relatively nonactive with the peroxide whitening agent in the nonaqueous liquid compositions. In various embodiments, the activator is operable to react with the peroxide to release oxygen when the liquid whitening composition applied to the teeth is contacted with saliva in the oral cavity. The peroxide activator is optionally present in embodiments of this invention at a concentration of about 0.1% to about 50%.

[0087] pH modifying agents among those useful herein include acidifying agents to lower pH, basifying agents to raise pH, and buffering agents to control pH within a desired range. For example, one or more compounds selected

from acidifying, basifying and buffering agents can be included to provide a pH of about 2 to about 10, or in various embodiments from about 2 to about 8, from about 3 to about 9, from about 4 to about 8, from about 5 to about 7, from about 6 to about 10, and from about 7 to about 9. Any orally acceptable pH modifying agent can be used, including without limitation carboxylic, phosphoric and sulfonic acids, acid salts (e.g., monosodium citrate, disodium citrate, monosodium malate, etc.), alkali metal hydroxides such as sodium hydroxide, carbonates such as sodium carbonate, bicarbonates, sesquicarbonates, borates, silicates, phosphates (e.g., monosodium phosphate, trisodium phosphate, pyrophosphate salts, etc.), imidazole and mixtures thereof. One or more pH modifying agents are optionally present in a total amount effective to maintain the composition in an orally acceptable pH range.

[0088] Mouth-feel agents include materials which impart a desirable texture or other feeling during use of the composition. Such agents include bicarbonate salts, which in various embodiments impart a "clean feel" to teeth and gums due to effervescence and release of carbon dioxide. Any orally acceptable bicarbonate can be used, including without limitation alkali metal bicarbonates such as sodium and potassium bicarbonates, ammonium bicarbonate, and mixtures thereof. One or more bicarbonate salts are optionally present in a total amount of 0.1% to about 50%, for example about 1% to about 20%.

[0089] Flavorants among those useful herein include any material or mixture of materials operable to enhance the taste of the composition. Any orally acceptable natural or synthetic flavorant can be used, such as flavoring oils, flavoring aldehydes, esters, alcohols, similar materials, and combinations thereof. Flavorants

include vanillin, sage, marjoram, parsley oil, spearmint oil, cinnamon oil, oil of wintergreen (methylsalicylate), peppermint oil, clove oil, bay oil, anise oil, eucalyptus oil, citrus oils, fruit oils and essences including those derived from lemon, orange, lime, grapefruit, apricot, banana, grape, apple, strawberry, cherry, pineapple, etc., bean- and nut-derived flavors such as coffee, cocoa, cola, peanut, almond, etc., adsorbed and encapsulated flavorants, and mixtures thereof. Also encompassed within flavorants herein are ingredients that provide fragrance and/or other sensory effect in the mouth, including cooling or warming effects. Such ingredients include methol, menthyl acetate, menthyl lactate, camphor, eucalyptus oil, eucalyptol, anethole, eugenol, cassia, oxanone, α-irisone, propenyl guaiethol, thymol, linalool, benzaldehyde, cinnamaldehyde, N-ethyl-p-menthan-3-carboxamine, N,2,3-trimethyl-2-isopropylbutanamide, 3-1-menthoxypropane-1,2-diol, cinnamaldehyde glycerol acetal (CGA), methone glycerol acetal (MGA) and mixtures thereof. One or more flavorants are optionally present in a total amount of about 0.01% to about 5%, optionally in various embodiments from about 0.05 to about 2%, from about 0.1% to about 2.5%, and from about 0.1 to about 0.5%.

[0090] Sweeteners among those useful herein include orally acceptable natural or artificial, nutritive or non-nutritive sweeteners. Such sweeteners include dextrose, polydextrose, sucrose, maltose, dextrin, dried invert sugar, mannose, xylose, ribose, fructose, levulose, galactose, corn syrup (including high fructose corn syrup and corn syrup solids), partially hydrolyzed starch, hydrogenated starch hydrolysate, sorbitol, mannitol, xylitol, maltitol, isomalt, aspartame, neotame, saccharin and salts thereof, sucralose, dipeptide-based intense sweeteners,

cyclamates, dihydrochalcones and mixtures thereof. One or more sweeteners are optionally present in a total amount depending strongly on the particular sweetener(s) selected, but typically at levels of from about 0.005% to about 5%, optionally from about 0.01 to about 1%.

[0091] Colorants among those useful herein include pigments, dyes, lakes and agents imparting a particular luster or reflectivity such as pearling agents. In various embodiments, colorants are operable to provide a white or light-colored coating on a dental surface, to act as an indicator of locations on a dental surface that have been effectively contacted by the composition, and/or to modify appearance, in particular color and/or opacity, of the composition to enhance attractiveness to the consumer. Any orally acceptable colorant can be used, including talc, mica, magnesium carbonate, calcium carbonate, magnesium silicate, magnesium aluminum silicate, silica, titanium dioxide, zinc oxide, red, yellow, brown and black iron oxides, ferric ammonium ferrocyanide, manganese violet, ultramarine, titaniated mica, bismuth oxychloride, FD&C dyes, and mixtures thereof. One or more colorants are optionally present in a total amount of about 0.001% to about 20%, for example about 0.01% to about 10% or about 0.1% to about 5%.

[0092] In one embodiment, the present invention provides compositions comprising:

a) from about 0.5% to about 60% of an active, preferably a peroxide composite comprising hydrogen peroxide and an N-vinyl heterocyclic polymer;

b) from about 0.2% to about 60% of an acrylic acid polymer comprising a copolymer of a first monomeric unit selected from the group consisting of

acrylic acid, methacrylic acid, and combinations thereof, with a second monomeric unit selected from the group consisting of acrylates, acrylamides, acetates, and combinations thereof; and

(c) from about 0.5% to about 99.5% of ethyl alcohol.

Optionally, the composition additionally comprises one or more components including from about 1 to about 50 of % of a block copolymer of ethylene oxide and propylene oxide, from about 1% to about 30% of a petrolatum, from about 1% to about 40% of polyvinylpyrrolidone, and from about 1% to about 40% of hydrogen peroxide.

Methods of Manufacture

[0093] The compositions of the present invention are made by any variety of methods, including adding and mixing the ingredients of the composition in a suitable vessel such as a stainless steel tank provided with a mixer. In one embodiment, the composition components are added to the mixing vessel in the following order: adhesive polymer, diluent, thickener ingredients, peroxide composite (or other active) and any flavoring, colorant or sweetener. In one embodiment, the adhesive polymer is dissolved in ethyl alcohol at room temperature. Pluraflo L4370 and petrolatum are then added and the solution is mixed for five minutes. The peroxide or other active is added and the solution is mixed for 20 minutes until the mixture is homogenous. Additional ingredients such as flavorant, coloring or sweeteners are added at any point during the mixing process but in various embodiments, such ingredients are preferably added last or close to last.

Methods

[0094] The present invention provides methods for whitening a tooth surface using compositions according to the present invention. As referred to herein, "tooth" or "teeth" refers to natural teeth, dentures, dental plates, fillings, caps, crowns, bridges, dental implants, and the like, and any other hard surfaced dental prosthesis either permanently or temporarily fixed within the oral cavity. As used herein, "whitening" refers to a change in visual appearance of a tooth, preferably such that such that the tooth has a brighter shade. Increase in whiteness of a dental surface can be observed visually, for example with the aid of color comparison charts or gauges, or measured by colorimetry, using any suitable instrument such as a Minolta Chromameter, e.g., model CR-400 (Minolta Corp., Ramsey, NJ). The instrument can be programmed, for example, to measure Hunter Lab values or L*a*b* values according to the standard established by the International Committee of Illumination (CIE). The L*a*b* system provides a numerical representation of three-dimensional color space where L* represents a lightness axis, a* represents a red-green axis and b* represents a yellow-blue axis. The L* and b* axes are typically of greatest applicability to measurement of tooth whiteness. Increase in whiteness can be computed from differences in L*, a* and b* values before and after treatment, or between untreated and treated surfaces. A useful parameter is ΔE*, calculated as the square root of the sum of the squares of differences in L*, a* and b* values, using the formula:

$$\Delta E^* = [(\Delta L^*)2 + (\Delta a^*)2 + (\Delta b^*)2]1/2$$

A higher value of ΔE^* indicates greater increase in whiteness. In various embodiments, the method of the present invention can effect a ΔE^* of at least about 1, or at least about 3, or at least about 4, or at least about 5.

[0095] Accordingly, the present invention provides methods for whitening a tooth surface, comprising applying to the surface a safe and effective amount of a peroxide compound or peroxide complex and an acrylic acid polymer. Preferably the method comprises applying a composition of the present invention. As referred to herein, "applying" refers to any method by which the peroxide complex is placed in contact with the tooth surface. Such methods, in various embodiments, comprise direct application of a composition by such methods as rinsing, painting, and brushing. In various embodiments, application of the composition comprises the use of an application device which aids in maintaining contact of the complex to the tooth surface for sufficient time so as to allow whitening.

[0096] Suitable application devices include dental trays, mouthpieces, floss, fibers, chips, strips and tapes. Strips among those useful herein comprise polymers, natural and synthetic woven materials, non-woven material, foil, paper, rubber and combinations thereof. Preferably the strip of material is substantially water insoluble. Suitable polymers include polyethylene, ethylvinylacetate, polyesters, ethylvinyl alcohol, fluoroplastics, and combinations thereof In various embodiments, the strip of material is generally less than about 1 mm (millimeter) thick, optionally less than about 0.05 mm thick, optionally about 0.001 to about 0.03 mm thick. The shape of the strip is any shape and size that covers the desired oral surface. In one embodiment, the length of the strip material is from

about 2 cm (centimeter) to about 12 cm, in another embodiment from about 4 cm to about 9 cm. The width of the strip material will also depend on the oral surface area to be covered. The width of the strip is generally from about 0.5 cm to about 4 cm, in one embodiment from about 1 cm to about 2 cm. The strip material may comprise shallow pockets, optionally filled by a composition of this invention so as to provide reservoirs of peroxide complex. Strips among those useful herein are disclosed in U.S. Patent 6,514,484, Rajaiah et al. issued February 4, 2003.

[0097] In one preferred embodiment, the whitening composition is applied using a "paint on" technique. A small application device, such as a brush or spatula is coated with a composition of this invention and the composition is then placed on a tooth surface. Preferably, the composition be spread evenly on such surfaces, in sufficient quantity to deliver a whitening amount of the peroxide complex.

[0098] The present invention also provides methods for effecting the controlled release of an oxidizing peroxide species onto a tooth surface, comprising contacting the surface with a peroxide composite of the present invention. As referred to herein, such controlled release in various embodiments comprises sustained release of the peroxide complex. Without limiting the mechanism, function or utility of present invention, in some embodiments contact with saliva causes the release of an effective amount of peroxide active from the cross-linked polymer matrix to the applied tooth site over a period of time.. Preferably, the composition is contacted with the tooth surface for at least about 30 seconds, optionally at least about 1 minute.

[0099] In various embodiments, it is preferred that the subject does not eat or drink while the composition is in contact with the dental surface. The whitening composition can be removed as and when required, at will, by an employment of standard oral hygiene procedures such as brushing or by rinsing, e.g., with a mouthwash. The process can be repeated several times until the desired whitening results are achieved.

[0100] In various embodiments, compositions of the present invention are also used for the treatment or prevention of disorders in the oral cavity, including cavity prevention, whitening, plaque prevention or reduction, gingivitis prevention or reduction, tartar control, sensitivity prevention or reduction, breath malodor prevention or reduction, and stain prevention. Compositions of the present invention may also be used for the treatment or prevention of systemic disorders, such as the improvement of overall systemic health characterized by a reduction in risk of development of systemic diseases, such as cardiovascular disease, stroke, diabetes, severe respiratory infection, premature and low birth weight infants (including associated post-partum dysfunction in neurologic/developmental function), and associated increased risk of mortality. Such methods include those disclosed in U.S. Patent Publication 2003/0206874, Doyle et al., published November 6, 2003.

[0101] The present invention is further illustrated through the following non-limiting examples.

Example 1

[0102] A composition of the present invention is made, as follows:

Ingredients	**Weight %**
3M Silicone "Plus" Polymer VS 80	20
ethyl alcohol	35
cPVP-H_2O_2 powder	20
Pluraflo L4370	10
snow white petrolatum	15
Total (%)	100

[0103] The VS-80 adhesive polymer is dissolved in the ethyl alcohol. The Pluraflo and petrolatum are then added and the solution is mixed for five minutes. The peroxide is added and the solution is mixed for 20 minutes until the mixture is homogenous.

Example 2

[0104] A composition of the present invention is made, as follows:

Ingredients	**Weight %**
Luvimer 100P	18
ethyl Alcohol	35
cPVP-H_2O_2 powder	27
Pluraflo L4370	10
snow white petrolatum	10
Total (%)	100

[0105] The composition is made by a process generally as described above in Example 1.

Example 3

[0106] A composition of the present invention is made, as follows:

Ingredients	**Weight %**
Luvimer 100P	20
ethyl alcohol	35
cPVP-H_2O_2 powder	25
Pluraflo L4370	10
snow white petrolatum	10
Total (%)	100

[0107] The composition is made by a process generally as described above in Example 1.

Example 4

Ingredients	**Weight %**
3M Silicone "Plus" Polymer VS 80	20
Ethyl Alcohol	35
cPVP-H_2O_2 powder	20
Pluraflo L4370	10
snow white petrolatum	15
Total (%)	100

[0108] The composition is made by a process generally as described above in Example 1. The composition is subjected to accelerated aging (105/120) for several weeks, and remains stable with more than 90% of the peroxide remaining.

Example 5

[0109] A composition of the present invention is made, as follows:

Ingredients	**Weight %**
Poly HEMA	10
ethyl alcohol	20
urea peroxide	18
baking soda	1.5
tetrasodium pyrophosphate	1.5
propylene glycol	45
PVP K-90	1
fumed silica	3
Total (%)	100

[0110] The composition is made by a process generally as described above in Example 1. The whitening efficacy of the composition is determined using a duplicate pair of flow cells designed to accommodate a total of eight bovine enamel blocks (four in each cell). The bovine enamel blocks are stained using an established staining protocol (Indiana University, Indianapolis, IN). The initial L*, a* and b* values are matched as closely as possible using a chromometer (Minolta CR-321) based on initial L*, a* and b* values (CIELAB). These initial values are typically L* = 25.00, a* = 3.00, and b* = 5,000 to L* = 35.00, a* = 5.00, and b* = 7.00. The L, a, b values are measured four times at slightly differing locations on the surface of the bovine enamel blocks.

[0111] To simulate the saliva of the human mouth, an artificial saliva buffer solution maintained at 37°C is prepared which contains the salts usually present in saliva at levels typical to the levels found in human saliva. The bovine enamel blocks are placed in the flow cells and the compositions evenly applied using a brush, the amount of product applied is determined using the weight difference of the container. Flow over the teeth is 0.6 ml/min. for 30 min. Average initial (i) and

final (f) chromometer readings are used to calculate $\Delta E = ((L_f - L_i)_2 + (b_f - b_i)^2 + (a_f - a_i)^2)^{½}$. The final ΔE reported was the average overall observations after the rejection of outliers using the Student's test (95% confidence level). The results of the test, set forth in the following table, show that the composition has a whitening effect. The composition of this Example is tested accordingly, and is found to have a ΔE value of about 10.

Example 6

[0112] A composition of the present invention is made, as follows:

Ingredients	**Weight %**
Poly HEMA	10
ethyl alcohol	35
PVP-H_2O_2	15
baking soda	1.5
tetrasodium pyrophosphate	1.5
propylene glycol	36
PVP K-90	1
Total (%)	100

[0113] The composition is made by a process generally as described above in Example 1. The composition is tested, as described above, and is found to have a ΔE value of about 13.

What is Claimed Is:

1. An oral care composition, comprising:

   (a) a whitening agent; and

   (b) an acrylic film forming polymer.

2. An oral care composition according to Claim 1, wherein said acrylic acid polymer comprises a copolymer of a first monomeric unit selected from the group consisting of acrylic acid, methacrylic acid, and combinations thereof, with a second monomeric unit selected from the group consisting of acrylates, acrylamides, acetates, and combinations thereof.

3. An oral care composition according to Claim 2, wherein said polymer is a terpolymer comprising a combination of said second monomeric units.

4. An oral care composition according to Claim 2, wherein said first monomeric unit comprises methacrylic acid or ß-methacrylic acid.

5. An oral care composition according to Claim 4, wherein said second monomeric unit is selected from the group consisting of acrylates and combinations thereof.

6. An oral care composition according to Claim 4, wherein said second monomeric unit is selected from the group consisting of ethyl acrylate, butyl acrylate, N-tertbutyl acrylamide, and combinations thereof.

7. An oral care composition according to Claim 3, wherein said polymer additionally comprises a third monomeric unit selected from the group consisting of siloxanes, vinyl esters of $C_5 - C_{12}$ alcohols, and combinations thereof.

8. An oral care composition according to Claim 3, wherein said polymer is a terpolymer of t-butyl acrylate, ethyl acrylate, and methacrylic acid.

9. An oral care composition according to Claim 1, comprising from about 0.2% to about 60% of said polymer.

10. An oral care composition according to Claim 9, comprising from about 10% to about 30% of said polymer.

11. An oral care composition according to Claim 1, wherein said whitening agent comprises a peroxide compound selected from the group consisting of hydrogen peroxide, organic peroxy compounds, peroxy acids, and mixtures thereof.

12. An oral care composition according to Claim 11, wherein said peroxide compound comprises hydrogen peroxide.

13. An oral care composition according to Claim 12, wherein said peroxide compound comprises a complex of hydrogen peroxide and an N-vinyl heterocyclic polymer.

14. An oral care composition according to Claim 1, wherein said composition is substantially non-aqueous, and additionally comprises a lower alcohol.

15. An oral care composition according to Claim 14, additionally comprising an adhesion agent selected from the group consisting of silicone polymers, waxes, mineral oil, petrolatum, hydrophilic polymers, silicas, and mixtures thereof.

16. An oral care composition according to Claim 14, additionally comprising a hydrophilic polymer selected from the group consisting of polyethyelene glycols, nonionic polymers of ethylene oxide, block copolymers of ethylene oxide and propylene oxide, carboxymethylene polymers, polyvinyl pyrrolidone, and mixtures thereof.

17. An oral care composition according to Claim 14, additionally comprising a silicone polymer selected from the group consisting of silicone adhesives, silicone elastomers, silicone fluids, silicone resins, silicone gums and mixtures thereof.

18. An oral care composition, comprising:

(a) an active material; and

(b) an acrylic acid polymer comprising a copolymer of a first monomeric unit selected from the group consisting of acrylic acid, methacrylic acid, and combinations thereof, with a second monomeric unit selected from the group consisting of acrylates, acrylamides, acetates, and combinations thereof; and

(c) a lower alcohol.

19. An oral care composition according to Claim 18, wherein said first monomeric unit comprises methacrylic acid or ß-methacrylic acid.

20. An oral care composition according to Claim 19, wherein said second monomeric unit is selected from the group consisting of acrylates and combinations thereof.

21. An oral care composition according to Claim 20, wherein said second monomeric unit is selected from the group consisting of ethyl acrylate, butyl acrylate, N-tertbutyl acrylamide, and combinations thereof.

22. An oral care composition according to Claim 18, wherein said polymer is a terpolymer of t-butyl acrylate, ethyl acrylate, and methacrylic acid.

23. An oral care composition according to Claim 18, wherein said active material is selected from the group consisting of whitening agents, anticaries agents, tartar control agents, antiplaque agents, periodontal actives, abrasives, breath freshening agents, malodor control agents, tooth desensitizers, salivary stimulants, and combinations thereof.

24. An oral care composition according to Claim 23, wherein said peroxide compound comprises hydrogen peroxide.

25. An oral care composition according to Claim 24, wherein said peroxide compound comprises a composite of hydrogen peroxide and an N-vinyl heterocyclic polymer.

26. A method of delivering an oral care active, comprising applying to said surface a safe and effective amount of an oral care active and an acrylic acid polymer comprising a copolymer of a first monomeric unit selected from the group consisting of acrylic acid, methacrylic acid, and combinations thereof, with a second monomeric unit selected from the group consisting of acrylates, acrylamides, acetates, and combinations thereof.

27. A method according to Claim 26, wherein said oral care active is selected from the group comprising whitening agents, anticaries agents, tartar control agents, antiplaque agents, periodontal actives, abrasives, breath freshening agents, malodor control agents, tooth desensitizers, salivary stimulants, and combinations thereof.

28. A method according to Claim 27, wherein said oral care active is a whitening agent.

29. A method according to Claim 28, wherein said whitening agent comprises a peroxide compound.

30. A method according to Claim 26, wherein said first monomeric unit comprises methacrylic acid or ß-methacrylic acid.

31. A method according to Claim 26, wherein said second monomeric unit is selected from the group consisting of acrylates and combinations thereof.

32. A method according to Claim 31, wherein said second monomeric unit is selected from the group consisting of ethyl acrylate, butyl acrylate, N-tertbutyl acrylamide, and combinations thereof.

33. A method according to Claim 26, wherein said polymer is a terpolymer of t-butyl acrylate, ethyl acrylate, and methacrylic acid.

34. A method according to Claim 29, wherein said peroxide compound comprises hydrogen peroxide.

35. A method according to Claim 34, wherein said peroxide compound comprises a composite of hydrogen peroxide and an N-vinyl heterocyclic polymer.