Abbrégé/Abstract:
Oral care compositions containing agents that are effective for treating and modifying teeth and mucosal surfaces to be hydrophobic are disclosed. Hydrophobic modification of teeth and other oral cavity surfaces imparts a variety of end use benefits including prevention of caries, erosion, wear, staining, sensitivity and desquamation as well as providing shine, smoothness and positive tooth feel benefits. The compositions contain selected surface active organophosphate compounds that deposit and adhere to teeth and other oral cavity surfaces forming a hydrophobic coating having prolonged retention thereon. By forming a "hydrophobic coating" on the oral cavity surface is meant that the hydrophobic character of the surface is increased as measured, for example, by an increase of at least about 10 degrees in the water contact angle of the surface after treatment. The increased hydrophobic character of the surface is maintained for a period of at least about 5 minutes and desirably longer such as at least about 10, at least about 20 or at least about 30 minutes. The compositions may contain additional hydrophobic materials to further increase hydrophobicity of the surface and/or functionality of the coating to provide surface protection and many other benefits.
(54) Title: METHODS AND COMPOSITIONS FOR HYDROPHOBIC MODIFICATION OF ORAL CAVITY SURFACES

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METHODS AND COMPOSITIONS FOR HYDROPHOBIC MODIFICATION
OF ORAL CAVITY SURFACES

TECHNICAL FIELD

Compositions comprising selected surface active organophosphate compounds and use of these compositions for treating and modifying teeth and other oral cavity surfaces are provided. When applied to oral cavity surfaces, the present composition forms a substantially hydrophobic coating of the surface active organophosphate compound(s) on the treated surface. The organophosphate compound deposits on teeth and mucosal surfaces via bonds or linkages formed between the phosphate groups of the compound and cationic sites on the target surfaces. The treated surface is provided with increased hydrophobic character, which then imparts multiple end use benefits to that surface including ease of cleaning; increased retention of actives such as fluoride on teeth; and surface protection benefits, in particular improved resistance of teeth to bacterial or biofilm adhesion, erosive demineralization or dissolution, sensitivity and staining and prevention of tooth damage from subsequent exposure to erosive chemicals such as acidic foods and beverages. Appearance and textural benefits including smoothness, shine, glossiness, and clean tooth feel are also provided. The organophosphate may be used in combination with one or more other hydrophobic material to further increase hydrophobicity and/or improve functionality of the coating deposited on the surface.

BACKGROUND OF THE INVENTION

Oral care products such as toothpastes and mouthwashes are routinely used by consumers as part of their oral care hygiene regimens. Oral care products are formulated to provide both therapeutic and cosmetic hygiene benefits. Therapeutic benefits include caries prevention which is typically delivered through the use of various fluoride salts; gingivitis prevention by the use of antimicrobial agents such as triclosan, cetylpyridinium chloride, stannous fluoride, zinc citrate or essential oils; and hypersensitivity control through the use of ingredients such as strontium chloride, stannous fluoride or potassium nitrate. Cosmetic benefits include control of plaque and calculus formation, removal and prevention of tooth stain, tooth whitening, breath freshening, and overall improvements in mouth feel impression which can be broadly characterized as mouth feel aesthetics. For example, agents such as pyrophosphate salts have been used as antitartar agents and polymeric agents such as condensed phosphorylated polymers, polyphosphonates, and carboxylated polymers have been used in oral care compositions to provide benefits including
tooth surface conditioning and control of tartar, staining and astringency. To illustrate further, commonly assigned US 6,555,094 discloses oral care compositions comprising a stannous ion source, a fluoride ion source, and a polymeric mineral surface active agent such as polyphosphate that binds stannous, wherein the compositions provide effective antimicrobial activity for reducing plaque and gingivitis with minimal side effects of tooth staining and astringency. The compositions also provide reduction and control of supragingival calculus. Additional disclosures on the use of polyphosphate as mineral surface active agent in oral care compositions include commonly assigned US Patent Nos. 5,939,052; 6,187,295; 6,350,436; and 6,190,644.

Another benefit that is increasingly important for complete oral health is providing protection and resistance of teeth against erosion and wear, which is a permanent loss of tooth substance from the surface due to the action of chemicals, such as harsh abrasives and acids. Dental erosion may be caused by extrinsic or intrinsic factors. Extrinsic erosion is the result of oral consumption of dietary acids such as acidic beverages or fruit juices and environmental factors such as exposure to airborne contamination or acidic water in swimming pools. Intrinsic erosion is caused for example by endogenous acids produced in the stomach and which contact the teeth during the processes of vomiting, regurgitation or reflux. The main cause of regurgitation and induced vomiting are eating disorder conditions such as nervous vomiting, anorexia or bulimia (Moss, 1998, Int. Den. J., 48, 529).

The incidence and severity of dental erosion is on the rise with the increase in the consumption of acidic beverages and juices. The pH and titratable acidity of acidic beverages have been identified as the main causative agents in the initiation and progression of dental erosion (Lassi, 1995, Caries Res. 29, 349). Thus methods have been disclosed to modify acidic food and beverage products in order to prevent their erosive effect on teeth. See for example, commonly assigned US 5,108,761 and WO 01/52796; US 6,383,473; US 6,319,490; WO 01/72144; and WO 00/13531 all assigned to SmithKline Beecham; CA 1018393 assigned to General Foods Corp.; US 3,471613 and BE 638645, both assigned to Colonial Sugar Refining Co; and US 4,853,237 assigned to Sinebrychoff Oy. In addition there have been disclosures of oral care compositions comprising agents indicated to provide teeth with anti-erosion or acid resistance benefits including JP 2001/158725; US 4,363,794 and US 4,335,102 all assigned to Lion Corporation; US 5,130,123 to The University of Melbourne; WO 99/08550 and WO 97/30601 both to SmithKline Beecham; US 3,914,404 to Dow Chemical Co.; and commonly assigned US 3,105,798.
One mechanism to provide erosion protection and maintain tooth integrity is described in commonly assigned US Patent No. 6,685,920 by use of oral compositions comprising certain chemical agents that have affinity for the tooth surface. These agents either bind to the tooth surface or form insoluble compounds or complexes on the tooth surface, thereby forming a protective film or coating. Examples of useful agents are polymeric mineral surface active agents including phosphorylated polymers, such as polyphosphates that bind to teeth or metal ions such as stannous, zinc or copper that form insoluble compounds that deposit onto teeth, and combinations thereof. The polymeric coating or insoluble precipitate deposited onto teeth act as a protective layer that prevents erosive chemicals from contacting the tooth surface and etching away tooth hard tissue.

Another cause of tooth wear is abrasion which results when tooth surfaces rub against each other or when harsh abrasives are used for brushing or polishing teeth. When teeth are healthy and the enamel has not been compromised by demineralization or erosion, the level of wear caused by commercially available toothpastes is minimal and of little or no clinical consequence. However, if enamel has been demineralized and/or softened by exposure to an erosive challenge, the enamel becomes more susceptible to wear.

Caries is another condition that is detrimental to tooth health and structural integrity. The tooth caries process results in calcium phosphate mineral loss from tooth substrate induced by localized plaque microbiological acid production from fermentable dietary substrates. If left uninhibited, the caries process results in sufficient mineral loss from teeth, which manifests as a loss of structural integrity and the formation of a cavity. (G.H. Nancollas, “Kinetics of de- and re-mineralization,” pp 113-128; A. Thylstrup, J.D.B. Featherstone and L. Fredebo, “Surface morphology and dynamics of early enamel caries development,” pp 165-184 in: Demineralisation and Remineralisation of the Teeth, IRL Press Ltd., (1983). The caries process is not continuous but is described by cyclic periods of mineral loss from teeth, particularly following ingestion of fermentable carbohydrates, followed by periods of no mineral loss or even mineral repair of damaged local regions. Remineralization refers to the process of repair of acid damaged tooth structure – by the recrystallization of mineral salts on the tooth architecture. Remineralization processes are a natural protective feature of saliva against the formation of tooth cavities, as saliva is supersaturated with respect to calcium phosphate tooth mineral salts. Remineralization is accelerated by fluoride ions in solution which increase local supersaturation with respect to fluoridated calcium phosphate deposition. Fluoride uptake or fluoridation refers to the acquisition of fluoride into tooth substrates resulting from topical treatments with fluoride agents.
Often, but not always, remineralized teeth from treatments exhibit increases in fluoride uptake and retention. Demineralization is the process of mineral loss from teeth caused by plaque acids or dietary acids. Demineralization can occur on tooth surfaces or below tooth surfaces depending upon the composition of the acids, concentration and pH. Moreover teeth with increased remineralization and fluoride uptake and retention also exhibit superior resistance to acid demineralization. The processes of fluoride incorporation into teeth, remineralization and resistance to demineralization represent primary mechanisms toward the reduction of tooth decay or other acid insults. In addition to fluoride agents, it is also advantageous to incorporate antimicrobial agents in oral care compositions in order to control plaque bacteria and prevent plaque formation and acid production, which is a pre-requisite step of the caries process.

Together the caries process, abrasion, erosion and/or acid-mediated wear and loss of enamel are the primary etiological factors in the development of sensitivity or hypersensitivity problems. Dentinal hypersensitivity is a temporary induced pain sensation produced when hypersensitive teeth are subjected to changes in temperature and/or pressure or to chemical action. Hypersensitivity may occur when the dentin of a tooth is exposed, i.e., through loss of the protective enamel or cementum as described above. Dentin is a bone-like material in teeth that is usually covered by enamel above the gum line and cementum below the gum line. Dentin generally contains channels, called tubules, that allow material and energy transport between the exterior of the dentin and the interior of the tooth where the nerve is located. Exposure of these tubules to external stimuli can cause irritation of the nerve and lead to the discomfort or pain of hypersensitivity. Thus treatment of hypersensitivity generally involves making the nerve in the tooth less sensitive to stimuli or by blocking or occluding the tubules to prevent or limit exposure of the nerve to external stimuli.

Another problem associated with tooth wear and loss of enamel is development of irregularities, microcracks, crevices and general roughening of an otherwise smooth and even tooth surface, which naturally has a translucent white or slightly-off-white color and a shiny or lustrous appearance. The uneven tooth surface further promotes adsorption of particles, bacteria and staining agents onto the surface, which lead to proliferation of dental plaque, formation of calculus and discoloration, all contributing to an undesirable appearance. These changes to the surface affect the light scattering properties of the tooth surface, making it appear dull and discolored rather than white and having shine and luster.

Still another oral cavity problem affecting consumers is sensitivity to common ingredients in oral care products such as surfactants and tartar control agents, in particular condensed
polyphosphates such as pyrophosphate and hexametaphosphate, used to clean the oral cavity and prevent deposition of mineralized biofilms on hard tissue surfaces. The sensitivity to such cleaning agents is manifested by desquamation or sloughing off thin mucosal lining during the normal brushing process. While such desquamation is rather harmless since mucosa cells are quickly regrown and no significant pain is involved, the sloughed off tissue forms an unsightly residue in the mouth and lips.

The surfaces in the oral cavity are thus constantly exposed to endogenous and exogenous factors including plaque bacteria and acid, chemicals such as surfactants, harsh abrasives and oral care actives, dietary acids and staining agents that significantly impact the health and appearance of the oral cavity. While oral hygiene products are generally useful for cleaning and protecting the oral cavity from these factors, short term exposure and rapid clearance of actives from the oral cavity minimizes the longer term effects of actives contained in oral hygiene products. In addition, salivary composition, bacteria, and soft tissue abrasion further impacts retention of actives in the oral cavity. The above problems affect many consumers and there continues to be a search for more effective treatment and prevention options. The present invention is based on the discovery that compositions comprising agents that effectively modify teeth and other oral cavity surfaces to be hydrophobic provide protection against many undesirable conditions including bacterial adhesion, plaque, tartar, caries, erosion, sensitivity, tooth staining and desquamation. The present compositions also provide appearance and textural benefits including shine, smoothness and clean tooth feel.

SUMMARY OF THE INVENTION

The present invention provides oral care compositions comprising agents effective for treating and modifying teeth and mucosal surfaces to be hydrophobic, which then imparts end use benefits including prevention of caries, erosion, wear, staining, sensitivity and desquamation as well as providing shine, smoothness and positive tooth feel benefits. To impart hydrophobicity to teeth and other oral cavity surfaces, compositions are used comprising selected surface active organophosphate compounds that deposit and adhere to oral cavity surfaces forming a hydrophobic coating having prolonged retention thereon. By forming a “hydrophobic coating” on the oral cavity surface is meant that the hydrophobic character of the surface is increased as measured, for example, by an increase of at least about 10 degrees in the water contact angle of the surface after treatment. The increased hydrophobic character of the surface is maintained for a period of at least about 5 minutes and desirably longer such as at least about 10,
at least about 20 or at least about 30 minutes. The compositions may comprise additional hydrophobic materials to further increase hydrophobicity of the surface and/or functionality of the coating to provide surface protection and many other benefits.

These and other features, aspects, and advantages of the present invention will become evident to those skilled in the art from the detailed description which follows.

DETAILED DESCRIPTION OF THE INVENTION

While the specification concludes with claims particularly pointing out and distinctly claiming the invention, it is believed that the present invention will be better understood from the following description.

All percentages and ratios used herein are by weight of total composition, unless otherwise indicated. All percentages, ratios, and levels of ingredients herein are based on the actual amount of the ingredient, and do not include solvents, fillers, or other materials with which the ingredient may be combined as a commercially available product, unless otherwise indicated.

All measurements referred to herein are made at room temperature of about 25°C unless otherwise specified.

Herein, "comprising" means that other steps and other components may be added. This term encompasses the terms "consisting of" and "consisting essentially of."

As used herein, the words “include,” and “contain” and their variants, are intended to be non-limiting, such that recitation of items in a list is not to the exclusion of other items that may also be useful in the materials, compositions, devices, and methods of this invention.

As used herein, the words “preferred”, “preferably” and variants refer to embodiments 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.

By “oral care composition” is meant a product, which in the ordinary course of usage, is not intentionally swallowed for purposes of systemic administration of particular therapeutic agents, but is rather retained in the oral cavity for a time sufficient to contact substantially all of the dental surfaces and/or oral tissues for purposes of oral activity. The oral care composition may be in various forms including toothpaste, dentifrice, tooth gel, subgingival gel, mouthrinse, mousse, foam, denture care product, mouthspray, lozenge, chewable tablet or chewing gum. The oral care composition may also be incorporated onto floss, strips or films for direct application or
attachment to oral surfaces or integrated into a device or applicator such as a toothbrush or roll-on. Such applicators may be for single or multiple use.

The term “dentifrice”, as used herein, includes paste, gel, liquid, powder or tablet formulations unless otherwise specified. The dentifrice composition may be a single phase composition or may be a combination of two or more separate dentifrice compositions. The dentifrice composition may be in any desired form, such as deep striped, surface striped, multilayered, having a gel surrounding a paste, or any combination thereof. Each dentifrice composition in a dentifrice comprising two or more separate dentifrice compositions may be contained in a physically separated compartment of a dispenser and dispensed side-by-side.

The term “dispenser” means any pump, tube, or container suitable for dispensing compositions such as dentifrices.

The term “teeth” refers to natural teeth as well as artificial teeth or dental prosthesis.

The term “orally-acceptable carrier” refer to safe and effective materials and conventional additives used in oral care compositions collectively referred to as “oral care agents” and including but not limited to one or more of fluoride ion sources, anti-calculus or anti-tartar agents, antimicrobial agents, anti dry mouth agents, buffers, abrasives such as silica, alkali metal bicarbonate salts, thickening materials, humectants, water, surfactants, titanium dioxide, flavorants, sweetening agents, coolants and other sensates, xylitol, and coloring agents.

Active and other ingredients useful herein may be categorized or described by their cosmetic and/or therapeutic benefit or their postulated mode of action or function. However, it is to be understood that the active and other ingredients useful herein can, in some instances, provide more than one cosmetic and/or therapeutic benefit or function or operate via more than one mode of action. Therefore, classifications herein are made for the sake of convenience and are not intended to limit an ingredient to the particularly stated application or applications listed.

Herein, the terms "tartar" and "calculus" are used interchangeably and refer to mineralized dental plaque biofilms.

In accordance with the present invention, compositions are provided that comprise one or more organophosphate compounds to impart hydrophobicity to teeth and other oral surfaces. Suitable organophosphate compounds have a strong affinity particularly for the tooth surface and have sufficient surface binding propensity to desorb pellicle proteins and remain affixed thereon. The phosphate groups of the organophosphate attach themselves to cations, in particular calcium ions in teeth or other positively charged sites such as protein residues on the mucosal surface and thus serve to anchor the hydrophobic portion of the molecule onto the surface, thereby modifying
it to be hydrophobic. The phosphate groups readily bond to cationic and charged surfaces via electrostatic interaction, hydrogen bonding, or complexation, which leads to ready deposition of the organophosphate upon application to form a coating on the treated surface. The strong bond results in longer retention or durability and substantivity of the coating. The present invention provides oral care compositions that deposit a substantive hydrophobic coating on teeth or other oral surface that is retained for a sufficient period of time to deliver the desired benefit(s), particularly with repeated use. Advantageously, the present organophosphates can also act as a carrier for other active agents such as for example, antimicrobials and cosmetic ingredients, in particular those which are hydrophobic in nature, such as most flavor and fragrance ingredients, delivering such agents to the surface where they can perform their intended function.

The substantive hydrophobic coating functions as protective barrier to prevent access to tooth surfaces by bacteria, acids, food particles, staining agents, etc., and to prevent active agents deposited on the surface from being rapidly washed away. Specifically, the substantive nature of the coating means it is retained longer on the treated surface as opposed to being easily washed away. Substantivity is important because it allows for enduring protection and prolonged contact of the active agents with the surface being treated thereby enhancing the bleaching, antimicrobial, anticaries, taste or cooling sensation or other desired effect on the surface. For example, prolonged retention of antimicrobials on oral surfaces will result in reducing oral microorganisms that are causative of, or associated with, various dental diseases, including gingivitis, periodontal disease, and dental plaque. With respect to fluoride delivery from a daily use oral care composition such as dentifrice or mouthrinse, the present method of using a substantive hydrophobic coating to retain the fluoride that has been deposited thereon represents a means to increase remineralization and fluoride uptake into teeth, which lead to strengthening of the tooth structure and reduction of mineral loss and tooth decay. In another example, delivery and retention of coolants on oral surfaces provide long lasting fresh mouth feel.

In one aspect oral care compositions are provided, which comprise in an orally acceptable carrier from about 0.01% to about 35%, alternatively from about 0.035% to about 20%, alternatively from about 0.035% to about 10%, or alternatively from about 0.035% to about 5%, by weight of the total oral composition of an organophosphate compound, the compositions depositing a substantive hydrophobic coating on oral cavity surfaces, teeth in particular. By depositing a “ substantive hydrophobic coating” on a surface is meant that the hydrophobic character of the surface is increased as measured, for example, by an increase in the water contact angle of the surface of at least about 10 degrees and the increased hydrophobic character
is maintained for a period of at least about 5 minutes and desirably longer. For example, the water contact angle of dental enamel after treatment with a composition may increase by about 15 degrees or more depending on a number of factors including the chemical nature and solubility characteristics of the organophosphate, pH, the condition of the oral environment, and tooth surface characteristics.

Such increases in hydrophobic character of the surface have been found to correlate for example, with provision of protection from erosion due to acid or abrasive challenges. The hydrophobic coating and its protective benefit will last for a period of at least about 10 minutes and desirably much longer, for example at least about 30 minutes or at least about an hour or longer after use of the composition. Other benefits derived from the substantive hydrophobic coating include inhibition of bacterial adhesion and plaque build-up, stain removal and prevention of staining of natural teeth and dental prosthesis or dentures. Color bodies or staining materials such as polyphenolic compounds (catechols and tannins) are constituents of various dietary products such as tea, coffee, wine, cola and a variety of fruits and berries. Consumption of these dietary products is known to cause deposition of staining materials on teeth. When the present compositions are applied to the oral cavity such as by toothbrushing or by rinsing, a hydrophobic coating is deposited onto teeth. Thus when color bodies are introduced in the oral cavity, they contact the hydrophobic coating instead of the tooth surface, thereby preventing stain from forming on teeth. Adhesion of bacteria and plaque formation on teeth can also be prevented and the coating additionally inhibits the ability of plaque to absorb colored components from ingested products such as tea, beer, red wines, etc. and form stain on teeth.

Another benefit derived from depositing the present hydrophobic coating on teeth is improvement in tooth appearance and mouth feel, specifically providing shine, smoothness, clean tooth feel, lubricity and moisturized feel as opposed to a dry mouth feel. The present compositions form a coating on the tooth surface that conforms to the topography of the tooth, essentially filling in pits, fissures, cracks, and other irregularities resulting in an even, smooth surface. The coating remains in place until mechanically removed from these cracks, etc. and thereby provides extended protection benefits, since the coating is not easily removed in the ordinary course of abrasive action by the tongue, mastication of food, toothbrushing, etc.

Examples of suitable organophosphate compounds are mono-, di- or triesters represented by the following general structure wherein Z', Z^2, or Z^3 may be identical or different, at least Z^1 being an organic moiety preferably selected from linear or branched alkyl, alkenyl, alkoxylated alkyl or alkoxylated alkenyl group of from 6 to 22 carbon atoms or from 10 to 22 carbons,
optionally substituted by one or more phosphate groups; each of $Z^2$ and $Z^3$ represents hydrogen, alkali metal, ammonium, protonated alkyl amine, protonated alkanolamine, or a $Z^1$ group.

$$
\begin{aligned}
Z^1 & \longrightarrow \text{O} \longrightarrow \text{P} \longrightarrow \text{O} \longrightarrow Z^2 \\
& \downarrow \text{O} \longrightarrow Z^3
\end{aligned}
$$

Among suitable organophosphate compounds are alkoxylated alkyl or alkoxylated alkenyl phosphate esters represented by the following structure:

$$
\begin{aligned}
R^1 & \longrightarrow (\text{OC}_n\text{H}_{2n})_a(\text{OC}_m\text{H}_{2m})_b \longrightarrow \text{O} \longrightarrow \text{P} \longrightarrow \text{O} \longrightarrow Z^2 \\
& \downarrow \text{O} \longrightarrow Z^3
\end{aligned}
$$

wherein $R^1$ represents a linear or branched, alkyl or alkenyl group of from 6 to 22 carbon atoms, optionally substituted by one or more phosphate groups; $n$ and $m$, are individually and separately, 2 to 4; $a$ and $b$, individually and separately, are 0 to 20, $a+b$ is at least 1 and $Z^2$ and $Z^3$ may be identical or different, each represents hydrogen, alkali metal, ammonium, protonated alkyl amine or protonated functional alkyl amine such as an alkanolamine, or a $R^1-(\text{OC}_n\text{H}_{2n})_a(\text{OC}_m\text{H}_{2m})_b-$ group. In some embodiments, $R^1$ will desirably be an alkyl group of from 10 to 22 carbon atoms and $a$ and $b$ may each be no more than 10 ($a+b \leq 10$) in order to maintain overall hydrophobic character of the organophosphate and the degree of hydrophobicity imparted to the surface.

Examples of organophosphate compounds include mono-, di- and tri- alkyl or alkyl (poly)alkoxy phosphates such as dodecyl phosphate, lauryl phosphate; laurate-1 phosphate; laurate-3 phosphate; laurate-9 phosphate; dilaureth-10 phosphate; trilaureth-4 phosphate; C12-18 PEG-9 phosphate and salts thereof. Many are commercially available from suppliers including Croda; Rhodia; Nikkol Chemical; Sunjin; Alzo; Huntsman Chemical; Clariant and Cognis.

Particularly useful organophosphates herein are those that are compatible and stable with other components of oral care composition such as fluoride sources and antimicrobials such as cetylpyridinium chloride (CPC), dimiphen bromide and metal ions such as stannous, copper and zinc, thus permitting single phase formulations. Even more importantly, the organophosphate agent will not significantly interfere with the activity of other actives in the composition, specifically their fluoridation, mineralization and antimicrobial activities.

In some embodiments, the organophosphate will be used in combination with one or more hydrophobic materials to further increase hydrophobicity and/or improve functionality of the
coating deposited on the treated surface. The hydrophobic coating on the surface created by the organophosphate enables deposition of other hydrophobic material(s) resulting in increased hydrophobicity and/or modification of the coating such as for example in terms of continuity and thickness. A continuous hydrophobic coating would provide a more effective protective barrier as well as effectively fill in irregularities, cracks, and crevices on the tooth surface.

Hydrophobic materials useful herein include compounds that are generally non-polar and water-insoluble but may be water dispersible. By “water-insoluble” herein is meant the compound has a solubility in water of about 0.01% or less at 25°C. Suitable hydrophobic or water-insoluble materials include long chain hydrocarbon waxes and oils such as petrolatum and microcrystalline wax; fatty compounds including alcohols, ethers, acids and esters; silicone polymers; and fluoroorganopolymers. Such materials have been suggested for inclusion in oral hygiene preparations.

For example, oral compositions containing silicone oils such as polydimethylsiloxanes (PDMS) are described in U.S. Patent Nos. 5,032,387; 5,165,913; 5,057,308 all to Hill, et al. and in U.S. Patent No. 5,422,098 to Rolla et al. However, PDMS polymers have not generally been used successfully for coating the teeth because of poor adhesion and retention of the PDMS on tooth surfaces. To improve the adherence of the silicone on surfaces, it has been suggested to modify the silicone by addition of functional groups such as carboxy, anhydride, polyol and amino groups. Such modified silicones have been suggested for modifying various surfaces; including fibers, textiles, leather, hair and skin, teeth, paper, plastic, wood, metal, glass, stone and concrete. For example, aminoalkyl silicones are described in commonly assigned US Patent Nos. 6,153,567; 6,129,906 and 6,024,891; carboxy or anhydride group containing silicones are described in commonly assigned US Patent Nos. 7,025,950 and 7,166,235.

Hydrophobic or water-insoluble materials for use herein include long chain hydrocarbons, especially paraffins having a chain length of 16 carbons or greater; natural waxes of animal, vegetable or mineral origin such as beeswax, lanolin, spermaceti, and carnauba wax; and synthetic ethylenic polymers such as polymethylene wax (Paraflint), polybutene and polyisobutene. Also useful are various fluoroorganopolymers where some or all of the hydrogen are replaced by fluorine, including, among others; polytetrafluoroethylene (PTFE); fluorinated polyethylene-propylene (FEP); polyvinylidene fluoride (PVDF); and polyvinylfluoride (PVF). These hydrophobic materials and their use in oral care compositions are described for example in US Patent Nos. 5,665,333; 5,888,480 5,961,958; and 5,980,868 all to Homola et al. Oral care
compositions containing polybutene are disclosed e.g., in US Patent Nos. 6,514,484 and 6,719,995 to Rajaiah et al.

Suitable fatty compounds such as described in commonly assigned application published as US 2008/0081023, include those having a hydrophobic tail group $R_1$, which is an alkyl, alkenyl (containing up to 3 double bonds), alkyl aromatic, or branched alkyl group typically of C$_{12}$-C$_{20}$ length. Non-limiting examples of alkyl, alkenyl, or branched alkyl groups suitable for the fatty compounds of the present invention include lauryl, tridecyl, myristyl, pentadecyl, cetyl, heptadecyl, stearyl, arachidyl, behenyl, undecylenyl, palmitoleyl, oleyl, palmoveyl, linoleyl, linolenyl, arachidonyl, elaidyl, elaeostearyl, erucyl, isolauryl, isotridecyl, isomyristal, isopentadecyl, petroselinyl, isocetyl, isohexadecyl, isostearyl, isoarachidyl, isobehnynl, gadoleyl, brassidyl, and technical-grade mixture thereof. The alkyl, alkenyl or branched carbon chains may be of vegetable origin.

Suitable fatty compounds of the present invention may also have a hydrophilic head group which does not make the compound water soluble, such as in compounds having a hydrophilic lipophilic balance (HLB) of 6 or less. Non-limiting examples of classes of compounds having such a hydrophilic head group include fatty alcohols, alkoxylated fatty alcohols, fatty phenols, alkoxylated fatty phenols, fatty amides, alkoxylated fatty amides, fatty amines, fatty alkylamidoalkylamines, fatty alkoxyxylated amines, fatty carabamates, fatty amine oxides, fatty acids, alkoxylated fatty acids, fatty diesters, fatty sorbitan esters, fatty sugar esters, methyl glucoside esters, fatty glycol esters, mono, di and tri glycerides, polyglycerine fatty esters, alkyl glyceryl ethers, propylene glycol fatty acid esters, cholesterol, ceramides, fatty silicone waxes, fatty glucose amides, and phospholipids.

The following provides non-limiting examples of classes of compounds from which one or more fatty compounds suitable for use in the present invention may be selected.

a. Fatty Alcohols / Alkoxylated Fatty Alcohol Ethers according to the following formula:

$$R_1-(OR_2)_k-OH$$

wherein $R_1$ is as described above; $R_2$ is a C$_{1}$-C$_{5}$ carbon chain which may be branched or hydroxy substituted; and $k$ is a number ranging from about 0 to about 5.

The fatty alcohols useful herein typically have from about 12 to about 60 carbon atoms, alternatively from about 16 to about 60 carbon atoms. These fatty alcohols may be straight or branched chain alcohols and may be saturated or unsaturated. Non-limiting examples of suitable fatty alcohols include cetyl alcohol, stearyl alcohol, arachidyl alcohol, behenyl alcohol, eicosyl alcohol, C20-40 alcohols, C30-50 alcohols, C40-60 alcohols, and mixtures thereof.
Suitable alkoxylated fatty alcohol ethers include addition products of 1 to 5 mol of ethylene oxide with a linear fatty alcohol having about 12 to about 60 carbon atoms, which are all adducts obtainable by the known industrial oxyethylation processes. Also suitable are the polyethylene oxide condensates of alkyl phenols, for example, the condensation products of alkyl phenols having an alkyl group containing from about 12 to about 60 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, wherein the ethylene oxide is present in amounts equal to from about 1 to about 5 moles of ethylene oxide per mole of alkyl phenol. Further suitable alkoxylated fatty alcohol ethers include those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products.


b. Di-Fatty Ethers according to the following formula:

$$R_1-(OR_2)_k-Z-(R_2O)-R_1$$

wherein $R_1$ is as described above; $R_2$ is a C$_1$-C$_5$ carbon chain which can be branched or hydroxy substituted; $k$ and $l$ each is independently a number such that the sum ($k + l$) has a value ranging from 1 to 30; and $Z$ is an ether (i.e., -O-) or an amine (i.e., -NR$_2^-$, wherein $R_2$ is as described immediately above).

Non-limiting examples of suitable di-fatty ether compounds include dicetylstearl ether, dicetylstearyl dioxyethyl ether, and N,N-bis(2-cetylstearyl-oxyethyl)aminoethanol.

c. Fatty Amides / Fatty Alkanolamides / Fatty Alkoxylated Amides according to the following formula:

$$\begin{array}{c}
\text{O} \\
\text{R}_1 \text{-C-N} \\
\text{X} \\
(R_2O)_k \\
\text{Y}
\end{array}$$

wherein $R_1$ is as described above; $R_2$ and $R_3$ each is independently a C$_1$-C$_5$ carbon chain which can be branched or hydroxy substituted; $k$ and $l$ each is independently a number such that the sum ($k + l$) has a value ranging from 0 to 10; and $X$ and $Y$ are each independently selected from hydrogen, a C$_1$-C$_4$ carbon chain which can be branched or hydroxy substituted, morpholine, or a C$_5$-C$_50$ carbon chain bonded via an amide, ester, or ether linkage.

Non-limiting examples of suitable fatty amides, fatty alkanolamides or fatty alkoxylated amides include Cocamide, Cocamide Methyl MEA, Cocoyl Glutamic Acid, Erucamide,
Lauramide, Oleamide, Palmitamide, Stearamide, Stearyl Erucamide, Behenamide DEA, Behenamide MEA, Cocamide DEA, Cocamide MEA, Cocamide MIPA, Hydroxyethyl Stearamide-MIPA, Hydroxypropyl Bisisostearamide MEA, Hydroxypropyl Bislauramide MEA, Hydroxystearamide MEA, Isostearamide DEA, Isostearamide MEA, Isostearamide MIPA, Lauramide DEA, Lauramide MEA, Lauramide MIPA, Myristamide DEA, Myristamide MEA, Myristamide MIPA, Palmande DEA, Palmande MEA, Palmande MIPA, Palmitamide DEA, Palmitamide MEA, PEG-20 Cocamide MEA, Stearamide AMP, Stearamide DEA, Stearamide DEA-Distearate, Stearamide DIBA-Stearate, Stearamide MEA, Stearamide MEA-Stearate, Stearamide MIPA, PEG-2 Cocamide, PEG-3 Cocamide, PEG-4 Cocamide, PEG-5 Cocamide, PEG-6 Cocamide, PEG-7 Cocamide, PEG-3 Lauramide, PEG-5 Lauramide, PEG-3 Oleamide, PEG-9 Oleamide, PEG-4 Stearamide, PEG-10 Stearamide, PPG-2 Cocamide, PPG-2 Hydroxyethyl Cocamide, PPG-2 Hydroxyethyl Coco/Isostearamide, Ceramide 1, Ceramide 2, Ceramide 3, Ceramide 4, and Ceramide 5.

d. Fatty Carbamates according to the following formula:

\[
R_1-O-C-N(\frac{R_2O}{k})\cdots X
\]

\[
\frac{R_3O}{l}-Y
\]

wherein R₁ is as described above; R₂ and R₃ each is independently a C₁-C₃ carbon chain which can be branched or hydroxy substituted; k and l each is independently a number such that the sum (k + l) has a value ranging from 0 to 10; and X and Y each is independently selected from hydrogen, a C₁-C₄ carbon chain which can be branched or hydroxy substituted, morpholine, or a C₅-C₅₀ carbon chain bonded via an amide, ester, or ether linkage.

Non-limiting examples of suitable fatty carbamates include cetyl carbamate, stearyl carbamate, PEG-2 stearyl carbamate, PEG-4 stearyl carbamate, and behenyl carbamate.

e. Fatty Alkylamido Alkylamines according to the following formula:

\[
R_1-C-NH(CH_2)_n-N(\frac{R_2O}{k})\cdots X
\]

\[
\frac{R_3O}{l}-Y
\]

wherein R₁ is as described above; R₂ and R₃ each is independently a C₁-C₃ carbon chain which can be branched or hydroxy substituted; k and l each is independently a number such that the sum (k + l) has a value ranging from 0 to 10; X and Y each is independently selected from hydrogen, a C₁-C₄ carbon chain which can be branched or hydroxy substituted, morpholine, or a
C₅-C₅₀ carbon chain bonded via an amide, ester, or ether linkage; and n is a number ranging from about 1 to about 4.

Non-limiting examples of suitable fatty alkylamido alkylamine compounds include stearamidoethoxyl diethanolamine, stearamidopropyl morpholine, stearamidopropyl dimethylamine stearate, stearamidopropyl dimethylamine, stearamidoethyl diethyamine, stearamidoethyl diethanolamine, isostearamidomorpholine stearate behenamidopropyldimethylamine, behenamidopropydiothylamine, behenamidoethyldiethyl-amine, cocamidopropyl dimethylamine behenamidoethyldimethylamine, arachidamidopropyldimethylamine, arachidamido-propydiothylamine, arachidamidoethyldiethylamine, arachidamidoethyldimethylamine, and mixtures thereof.

f. Fatty Amines / Fatty Alkanolamines / Fatty Alkoxylated Amines according to the following formulas:

\[ R_1-N-R_{5}^5 \]

wherein \( R_1 \) is as described above; and \( R_{5}^5 \) and \( R_{5}^5 \) are independently hydrogen or a C₁-C₅ carbon chain which can be branched or hydroxy substituted,

\[ R_1-N-(R_2O)_k-X \]
\[ R_1-Z(CH_2)_n-N-(R_2O)_l-Y \]

wherein \( R_1 \) is as described above; \( R_2 \) and \( R_3 \) each is independently a C₁-C₅ carbon chain which can be branched or hydroxy substituted; \( k \) and \( l \) each is independently a number such that the sum \( (k + l) \) has a value ranging from 0 to 10; \( X \) and \( Y \) each is independently hydrogen, a C₁-C₄ carbon chain which can be branched or hydroxy substituted, morpholine, or a C₅-C₅₀ carbon chain bonded via amide, ester, or ether linkage; \( n \) is a number ranging from about 1 to about 4; and \( Z \) is an ether (i.e., -O-) or an amine (i.e., -NH-).

Primary, secondary, and tertiary fatty amines are useful. Suitable fatty alkoxylated amine compounds include addition products of ethylene oxide with a linear fatty alkylamine having 12 to 60 carbon atoms, all of which are adducts obtainable by known industrial processes and which are commercially available.

Non-limiting examples of suitable fatty amine and fatty alkoxylated amine compounds include diethyllauramine, dicocamine, dimethylcocamine amine cetamine, stearamine, oleamine, behenamine, dimethylbehenamine amine, diethylbehenamine, dibehenylamine N-lauryl

g. Fatty Amine Oxides according to the following formula:

\[
\begin{align*}
(R_2O)_k & \quad \text{X} \\
R_1 \quad Z \quad (CH_2)_n \quad \text{N} \quad \text{O} \\
(R_3O)_l & \quad \text{Y}
\end{align*}
\]

wherein Rₙ is as described above; R₂ and R₃ each is independently a C₁-C₅ carbon chain which can be branched or hydroxy substituted; k and l each is independently a number such that the sum (k + l) has a value ranging from 0 to 10; X and Y each is independently hydrogen, a C₁-C₄ carbon chain which can be branched or hydroxy substituted, morpholine, or a C₅-C₅₀ carbon chain bonded via an amide, ester, or ether linkage; Z is an ether (i.e., -O-) or an amide (i.e., -C(O)-NH-) linkage; and n is a number ranging from about 1 to about 4. In accord with known convention, the arrow in the above formula is representative of a semi-polar bond.


h. Fatty Acid / Alkoxylated Fatty Acid according to the following formula:

\[
\begin{align*}
O \\
\text{R}_1 \quad \text{C} \quad (\text{OR}_2)_k \quad \text{OH}
\end{align*}
\]

wherein Rₙ is as described above; R₂ is a C₁-C₅ carbon chain which can be branched or hydroxy substituted; and k is a number ranging from about 0 to about 5.
Non-limiting examples of suitable fatty acids and alkoxylated fatty acids include behenic acid, C10-40 hydroxyalkyl acid, C32-36 isoalkyl acid coconut acid, erucic acid, hydroxystearic acid, lauric acid, linoleic acid, myristic acid, oleic acid, palmitic acid, PEG-8 behenate, PEG-5 cocoate, PEG-10 cocoate, PEG-2 laurate, PEG-4 laurate PEG-6 laurate, PEG-8 laurate, PEG-9 laurate, PEG-10 laurate, PEG-7 oleate, PEG-2 stearate, PEG-3 stearate, PEG-4 stearate, PEG-5 stearate, PEG-6 stearate, PEG-7 stearate, PEG-8 stearate, PEG-9 stearate, PEG-10 stearate, polyglyceryl-2-PEG-4 stearate, PPG-2 isostearate, and PPG-9 laurate.

i. Fatty Esters according to the following formula:

\[
\text{R}_1\text{C}-(\text{OR}_2)_k \text{OR}_6
\]

wherein \( \text{R}_1 \) is as described above; \( \text{R}_2 \) is a C\(_{11}\)-C\(_5\) carbon chain which can be branched or hydroxy substituted; \( k \) is a number ranging from about 1 to about 5; and \( \text{R}_6 \) is a C\(_{11}\)-C\(_{40}\) carbon chain or an alkylcarbonyl (i.e., \( -\text{C}(\text{O})-\text{R}_7 \), wherein \( \text{R}_7 \) is a C\(_{11}\)-C\(_{40}\) carbon chain).

These suitable fatty esters include esters with hydrocarbyl chains derived from fatty acids or alcohols (e.g., mono-esters, polyhydric alcohol esters, and di- and tri-carboxylic acid esters).

The hydrocarbyl radicals of the fatty esters hereof may include or have covalently bonded thereto other compatible functionalities, such as amides and alkoxy moieties (e.g., ethoxy or ether linkages, etc.).

Non-limiting examples of suitable fatty ester compounds include isopropyl isostearate, hexyl laurate, isohexyl laurate, isohexyl palmitate, isopropyl palmitate, decyl oleate, isodecyl oleate, hexadecyl stearate, decyl stearate, isopropyl isostearate, dihexyldecyl adipate, lauryl lactate, myristyl lactate, cetyl lactate, oleyl stearate, oleyl oleate, oleyl myristate, lauryl acetate, cetyl propionate, and oleyl adipate.

Fatty ester compounds of the present invention also may be selected from those according to the following formula:

\[
\begin{align*}
&\text{R'}_8\text{C}-(\text{OR''}_2)_k \text{OR'}_{10} \\
&\text{R''}_8\text{C}-(\text{OR'''}_2)_k \text{OR''}_{10} \\
&\text{R'''}_8\text{C}-(\text{OR''''}_2)_k \text{OR'''}_{10}
\end{align*}
\]

wherein \( \text{R'}_8 \), \( \text{R''}_8 \), and \( \text{R'''}_8 \) each is independently selected from hydrogen, hydroxy, or a C\(_{11}\)-C\(_4\) carbon chain which can be branched or hydroxy substituted; \( k', k'' \), and \( k''' \) each is
independently a number such that the sum \((k' + k'' + k''')\) has a value ranging from 0 to 15; \(R_2^\prime\), \(R_2^\prime\prime\), and \(R_2^\prime\prime\prime\) each is independently selected from a \(C_1-C_5\) carbon chain which can be branched or hydroxy substituted; and where \(R_{10}^\prime\), \(R_{10}^\prime\prime\), \(R_{10}^\prime\prime\prime\) each is independently selected from hydrogen or \(R_1\), where \(R_1\) is as defined above, provided that at least one of \(R_{10}^\prime\), \(R_{10}^\prime\prime\), and \(R_{10}^\prime\prime\prime\) is a \(R_1\) group.

Still other suitable fatty esters are di- and tri-alkyl and alkenyl esters of carboxylic acids, such as esters of \(C_4\) to \(C_8\) dicarboxylic acids (e.g., \(C_1\) to \(C_{22}\) esters or \(C_1\) to \(C_6\) esters of succinic acid, glutaric acid, and adipic acid). Specific non-limiting examples of di- and tri-alkyl and alkenyl esters of carboxylic acids include isocetyl stearyl stearate, stearyl citrate, distearyl citrate and tristearyl citrate.

Other useful fatty ester compounds are represented by the following formula:

\[
\begin{align*}
R_8^\prime & - C - O - (R_2O)_k^\prime - R_9^\prime \\
R_8^\prime & - C - O - (R_2O)_k^\prime - R_9^\prime \\
R_8^\prime & - C - O - (R_2O)_k^\prime - R_9^\prime 
\end{align*}
\]

wherein \(R_2^\prime\), \(R_2^\prime\prime\), and \(R_2^\prime\prime\prime\) each is independently selected from a \(C_1-C_5\) carbon chain which can be branched or hydroxy substituted; \(R_8^\prime\), \(R_8^\prime\prime\), and \(R_8^\prime\prime\prime\) each is independently selected from hydrogen, hydroxy, or \(C_1\) to \(C_4\) carbon chain which can be branched or hydroxy substituted; \(k'\), \(k''\), and \(k'''\) each is independently a number such that the sum \((k' + k'' + k''')\) has a value ranging from 0 to 15; and \(R_9^\prime\), \(R_9^\prime\prime\), and \(R_9^\prime\prime\prime\) each is independently selected from hydrogen or alkylcarbonyl (i.e., \(-C(O)\)\(\rightarrow\)\(R_1\), wherein \(R_1\) is as described above), provided that at least one of \(R_9^\prime\), \(R_9^\prime\prime\), and \(R_9^\prime\prime\prime\) is a \(-C(O)\)\(\rightarrow\)\(R_1\) group.

Other suitable fatty esters are those known as polyhydric alcohol esters. Such polyhydric alcohol esters include alkylene glycol esters, such as ethylene glycol mono and di-fatty acid esters, diethylene glycol mono- and di-fatty acid esters, polyethylene glycol mono- and di-fatty acid esters, propylene glycol mono- and di-fatty acid esters, polypropylene glycol monooelate, propylene glycol 2000 monostearate, ethoxylated propylene glycol monostearate, glyceryl mono- and di-fatty acid esters, polyglycerol poly-fatty acid esters, ethoxylated glyceryl monostearate, 1,3-butylene glycol monostearate, 1,3-butylene glycol distearate, polyoxyethylene polyol fatty acid ester.

Still other fatty esters suitable for use in the compositions of the present invention are glycerides, including, but not limited to, mono-, di-, and tri-glycerides. For use in the
compositions described herein, examples of glycerides are the mono-, di-, and tri-esters of glycerol and long chain carboxylic acids, such as C_{12} to C_{22} carboxylic acids. A variety of these types of materials can be obtained from vegetable and animal fats and oils, such as castor oil, safflower oil, cottonseed oil, corn oil, olive oil, cod liver oil, almond oil, avocado oil, palm oil, sesame oil, lanolin and soybean oil. Synthetic oils include, but are not limited to, triolein and tristearin glyceryl dilaurate.

j. Fatty Phosphorus Compounds according to the following formula:

\[
\begin{align*}
  &R_1-(R_2)_k-O-P-O \rightarrow O \\
  &R_5\quad \quad \quad \quad \\
\end{align*}
\]

wherein \(R_1\) is as described above; \(R_2\) is a C_{1}-C_5 carbon chain which can be branched or hydroxy substituted; \(k\) is a number ranging from about 0 to about 5; and \(R_5\) is hydrogen or a C_{1}-C_4 carbon chain which can be branched or hydroxy substituted. In accord with known convention, the arrow in the above formula is representative of a semi-polar bond.

Non-limiting examples of suitable fatty phosphorus compounds include dodecyl(dimethyl)phosphine oxide, tetradecyl(dimethyl)phosphine oxide, tetradecylmethyl(ethyl)phosphine oxide, 3,6,9-trioxaodecyl(dimethyl)phosphine oxide, cetyl(dimethyl)phosphine oxide, 3- dodecoxy-2-hydroxypropyl(di2-hydroxyethyl) phosphine oxide, stearyl(dimethyl)phosphine oxide, cetyl(ethyl)phosphine oxide, oleyl(diethylphosphine oxide, docosyl(diethylphosphine oxide, tetradecyl(diethylphosphine oxide, dodecyl(diethylphosphine oxide, dodecyldi(hydroxymethyl)phosphine oxide, dodecyldi(2-hydroxyethyl) phosphine oxide, tetradecylmethyl(2-hydroxypropyl)phosphine oxide, oleyldimethylphosphine oxide, and 2-hydroxydocosyl(dimethyl)phosphine oxide.

k. Fatty Sorbitan Derivatives according to the following formula:

\[
\begin{align*}
  &R^*_2O)_k \rightarrow R^* \quad \quad \quad \quad \\
  &O-(R^*_{-2})_k \rightarrow R^* \quad \quad \\
  &O-(R^*_{-2})_k \rightarrow R^* \quad \quad \\
  &O-(R^*_{-2})_k \rightarrow R^* \quad \quad \\
  &R^*^* \quad \quad \quad \quad \\
\end{align*}
\]

wherein \(R^*\), \(R^*\), \(R^*\), \(R^*\), \(R^*\) and \(R^*\) each is independently a C_{1}-C_5 carbon chain which can be branched or hydroxy substituted; \(R^*\), \(R^*\), \(R^*\), \(R^*\) and \(R^*\) each is independently hydrogen or
alkylcarbonyl (i.e., $-\text{C}(\text{O})\text{--R}_1$, wherein $\text{R}_1$ is as described above), provided that at least one of $\text{R}''_9$, $\text{R}'''_9$, $\text{R}''''_9$, and $\text{R}'''''_9$ is a $-\text{C}(\text{O})\text{--R}_1$ group; and $k'$, $k''$, $k'''$, and $k''''$ each is independently a number such that the sum $(k' + k'' + k''' + k''''$) has a value of from 0 to 20.

Non-limiting examples of suitable fatty sorbitan derivatives include PEG-20 sorbitan cocoate, PEG-2 sorbitan isostearate, PEG-5 sorbitan isostearate, PEG-20 sorbitan isostearate, PEG-10 sorbitan laurate, PEG-3 sorbitan oleate, PEG-6 sorbitan oleate, PEG-20 sorbitan oleate, PEG-3 sorbitan stearate, PEG-4 sorbitan stearate, PEG-6 sorbitan stearate, PEG-4 sorbitan triisostearate, PEG-20 sorbitan triisostearate, PEG-2 sorbitan trioleate, PEG-3 sorbitan tristearate, polyglyceryl-2 sorbitan tetraclylhexanoate, sorbitan caprylate, sorbitan cocoate, sorbitan diisostearate, sorbitan dioleate, sorbitan distearate, sorbitan isostearate, sorbitan laurate, sorbitan oleate, sorbitan olivate, sorbitan palmitate, sorbitan sesquisostearate, sorbitan sesquioleate, sorbitan sesquistearate, sorbitan stearate, sorbitan triisostearate, sorbitan tristearate, and sorbitan undecylate.

1. Sucrose Polyesters according to the following formula:

![Sucrose Polyesters formula](image)

wherein $\text{R}''_9$, $\text{R}'''_9$, $\text{R}''''_9$, $\text{R}'''''_9$, $\text{R}''''''_9$, and $\text{R}'''''''_9$ each is hydrogen or alkylcarbonyl (i.e., $-\text{C}(\text{O})\text{--R}_1$, wherein $\text{R}_1$ is as described above), provided that at least one of $\text{R}''_9$, $\text{R}'''_9$, $\text{R}''''_9$, $\text{R}'''''_9$, $\text{R}''''''_9$, and $\text{R}'''''''_9$ is a $-\text{C}(\text{O})\text{--R}_1$ group.

Non-limiting examples of suitable sucrose polyester compounds include Sucrose Coccoate, Sucrose Dilaurate, Sucrose Distearate, Sucrose Hexaerucate, Sucrose Hexaoleate/Hexapalmiitate/Hexastearate, Sucrose Hexapalmiitate, Sucrose Laurate, Sucrose Mortierellate, Sucrose Myristate, Sucrose Octaacetate, Sucrose Oleate, Sucrose Palmitate, Sucrose Pentaoerucate, Sucrose Polybehenate, Sucrose Polycottonseedate, Sucrose Polyolaurate, Sucrose Polyinoleate, Sucrose Polyooleate, Sucrose Polypalmate, Sucrose Polysoyate, Sucrose Polysteate, Sucrose Ricinoleate, Sucrose Stearate, Sucrose Tetraisostearate, Sucrose Tetrastearate Triacetate, Sucrose Tribenenate, and Sucrose Tristearate.
m. Alkyl Sulfoxides according to the following formula:

\[
\begin{align*}
(R_2O)_k \underrightarrow{X} \\
R_1 \underrightarrow{S} \rightarrow O
\end{align*}
\]

wherein \( R_1 \) is as described above; \( R_2 \) is a \( C_1-C_5 \) carbon chain which can be branched or hydroxy substituted; \( k \) is a number ranging from about 0 to about 10; and \( X \) and \( Y \) each is independently selected from hydrogen or a \( C_1-C_4 \) carbon chain which can be branched or hydroxy substituted.

Non-limiting examples of suitable alkyl sulfoxide compounds include octadecyl methyl sulfoxide, 2-ketotridecyl methyl sulfoxide, 3,6,9-trioxaoctadecyl 2-hydroxyethyl sulfoxide, dodecyl methyl sulfoxide, oleyl 3-hydroxypropyl sulfoxide, tetradecyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, and 3-hydroxy-4-dodecoxybutyl methyl sulfoxide.

The hydrophobic material added in combination with the organophosphate may be incorporated in the present dentifrice, rinse, denture cleanser, chewing gum and the like compositions at about 0.5% to about 20% by weight or from about 0.5% to about 5% by weight. Greater amounts up to about 90% may be used for oral gels such as paint-on or leave-on finishing or sealing gels or for denture adhesives.

Evaluation of Activity of Compositions

A water contact angle method is used to determine the degree of hydrophobicity imparted by the present compositions to tooth surfaces. Repeated measurements show increased contact angle from baseline indicating a tendency of the surface to repel water, i.e., increased hydrophobicity following treatment with the present compositions. The method uses polished bovine enamel chips that are cleaned using a prophylactic paste followed by an acetone wipe and water rinse in a sonicator. Chips are then allowed to air dry for 60-90 minutes, and then baseline water contact angles are measured using Drop Shape Analysis System DSA 10 – MK2 from KRUSS. Chips with baseline water contact angle of about 48.00 ± 5.00 are selected and randomized into groups of three per treatment. Following randomization each group of three chips are treated with a solution or dentifrice slurry (1:3 ratio) containing the test ingredient followed by a water rinse. The chips are then soaked in human saliva for an hour at 37°C. After the saliva soak, the chips are removed, rinsed with water and air dried. Contact angle reading is taken after at least 2 hours of drying. Water or regular toothpaste (without organophosphate) are used as controls. The post-treatment contact angle is subtracted from the baseline contact angle. An increase in contact angle (post-treatment value – baseline) represents increased hydrophobic character of the surface; a decrease represents increased hydrophilic character of the surface.
One method to determine the surface protection benefit of hydrophobic modification is by measuring the effects on hydroxy apatite (HAP) powder, a synthetic analog of enamel and dentine, as a substrate. In this protocol, HAP powder is pretreated with dentifrice slurry supernatant (20 g supernatle/200mg HAP powder) followed by three times washing with water. After the last wash, 2 ml of water is added and vortexed to form a uniform slurry. In a separate beaker, 25 ml of 0.1M acetate buffer is prepared and pH adjusted to 4.5. To this buffer solution having initial pH of 4.5, a sample of 0.5ml of pre-treated HAP slurry is added and dissolution profile of the pretreated HAP powder is monitored via changes in pH of the acetate buffer solution. The pH change is measured and recorded using a Brinkman Titrino titrator device for 30 minutes. With HAP dissolusion, pH increases and the pH change is compared to that of a plain water treated HAP as control and is used to calculate percent inhibition of HAP mineral loss.

Another method to evaluate surface protection benefits such as in terms of inhibiting mineral surface loss from exposure to acid uses the following in vitro erosion cycling protocol.

Tooth (dentin or enamel) specimens are prepared by cutting 3mm - 4mm cores from extracted, human teeth using a diamond core drill. The teeth, collected by local surgeons, are stored until use in a 5% Thymol solution maintained at room temperature. Specimens are mounted on lucite rods with a dental acrylic (Dura Base, Reliance Mfg. Co.) covering all sides except the surface. Course polishing with 600-grit silicon carbide-water slurry is used to remove approximately 50 microns of the outer specimen surface to ensure homogeneity among specimens. Specimens are then polished with gamma alumina (Buehler No. 3, B Gamma Micropolish Alumina) to a mirror-like finish.

Approximately 2/3 of the surface of each specimen is then covered with an acid resistant nail polish (placed in a mesial-distal fashion), leaving the center portion exposed as a treatment window. Covered portions remain covered with the acid-resistant nail polish throughout the experiment, serving as the control (untreated) areas for later microradiographic analysis. Specimens are randomly assigned to one of four treatment groups (4 specimens/group).

Each group of specimens is placed in 20 ml of fresh, pooled human saliva for at least one hour to form an initial layer of pellicle on the specimen surfaces prior to first day of treatment. To begin the treatment phase, aqueous solutions of the test organophosphates and dentifrice slurry (1:3) of the control fluoride toothpaste are prepared in fresh, pooled human saliva. Each treatment cycle consists of: dentifrice slurry (2 min) → rinse in deionized distilled H2O → saliva (1 hour) → erosion challenge (10 min) → rinse in ddH2O → saliva. There are 4 treatments per day for a total of five treatment days. Dentifrice treatments consist of immersing the specimens
into the dentifrice slurry for two minutes while specimens rotate at 75 rpm. The erosion challenge consists of soaking each treatment group in 12 ml of 1% Citric acid (at room temperature). At any time specimens are not in treatment, they remain in 20 ml of pooled, human saliva (stirred). The saliva is refreshed 3X/day. At night, each group of specimens remains immersed in saliva (stirred at room temperature).

After 5 days of treatment, thin cross-sections (80 – 120μm thick) of each specimen are removed for assessment using standardized transverse microradiography (TMR) techniques. The exposed, treated area of each specimen is assessed with respect to complete mineral loss (erosion). Results are recorded as depth (in microns μ) of total mineral loss from the original specimen surface using the covered (untreated) areas as anatomical reference points. For comparison, percent reduction in surface mineral loss is calculated relative to control compositions (water or fluoride containing compositions without the organophosphate).

Results of testing various organophosphates compounds alone and in combination with other hydrophobic materials and oral care agents are presented in the following tables.

Table 1. Change in Water Contact Angle of Enamel Surface and Inhibition of Hydroxyapatite (HAP) Powder Surface Loss

<table>
<thead>
<tr>
<th>(1) Treatment</th>
<th>Δ Water Contact Angle</th>
<th>% Inhibition of HAP Surface Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% Potassium Laureth Phosphate</td>
<td>45.43</td>
<td>89.7</td>
</tr>
<tr>
<td>1% Potassium Laureth Phosphate + 1% Tergitol™</td>
<td>25.3</td>
<td>51.4</td>
</tr>
<tr>
<td>1% Potassium Laureth Phosphate + 1% SLS</td>
<td>-</td>
<td>86.6</td>
</tr>
<tr>
<td>1% Sodium Dodeceth-1 Phosphate</td>
<td>32.13</td>
<td>94.5</td>
</tr>
<tr>
<td>1% Sodium Dodeceth-1 Phosphate + 1% CAPB</td>
<td>13.1</td>
<td>-</td>
</tr>
<tr>
<td>1% Sodium Dodeceth-1 Phosphate + 1% Tergitol™</td>
<td>21.97</td>
<td>89.6</td>
</tr>
<tr>
<td>1% Potassium Laureth-3 Phosphate</td>
<td>23.2</td>
<td>94.8</td>
</tr>
<tr>
<td>1% Potassium Laureth-3 Phosphate + 1% SLS</td>
<td>28.03</td>
<td>88.6</td>
</tr>
<tr>
<td>1% Potassium Laureth-3 Phosphate + 1% Tergitol™</td>
<td>22.97</td>
<td>79.0</td>
</tr>
<tr>
<td>1% Sodium Dodeceth-9 Phosphate</td>
<td>16.43</td>
<td>45.24</td>
</tr>
<tr>
<td>1% Sodium Dodeceth-9 Phosphate + 1% SLS</td>
<td>17.87</td>
<td>53.9</td>
</tr>
<tr>
<td>1% Sodium Dodeceth-9 Phosphate + 1% CAPB</td>
<td>16.7</td>
<td>-</td>
</tr>
<tr>
<td>1% Sodium Dodeceth-9 Phosphate + 1% Tergitol™</td>
<td>18.73</td>
<td>38.25</td>
</tr>
<tr>
<td>1% Tergitol™</td>
<td>0.0</td>
<td>2.52</td>
</tr>
<tr>
<td>1% SLS</td>
<td>0.23</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2: Effect of Organophosphate Concentration on Surface Modification and Protection from Acid Challenge
Table 1 shows the change in water contact angle of the surface from baseline after treatment and protective benefit against acid attack derived from the surface modification. Organophosphate compounds with C12 or longer alkyl chains provide effective hydrophobic modification of the tooth surface and protection benefits. The longer alkyl chains increase surface hydrophobicity and surface protection benefits. Compounds containing hydrophilic groups, e.g., a high degree of ethoxylation, provide relatively less hydrophobic surfaces; however, the degree of hydrophobic surface modification is sufficient to provide protection against acid attack and other insults. The data below show that there is significantly less tooth mineral surface loss from acid exposure when teeth were treated with compositions containing an alkyl phosphate (such as Sodium dodecyl phosphate) or alkyl ethoxy phosphate (e.g., Sodium laureth-1 phosphate or Sodium laureth-9 phosphate). The magnitude of surface protection effect depends on the structure and concentration of the organophosphate and the corresponding reactivity in solution and with the enamel surface. The presence of a single ethoxy group in the compound does not appear to significantly affect the degree of hydrophobicity imparted to the surface and surprisingly even increased the surface protection benefit. However, compounds with a higher average degree of ethoxylation (n ≥ 3) may provide less hydrophobicity and less surface protection. Herein the recited degree of alkoxylation, such as ethoxylation is an average number. For example, an average degree of ethoxylation of 9 means that the sample may contain a mixture of molecules with 9, less than 9 and more than 9 ethoxy groups.

The presence of certain co-surfactants, e.g., sodium lauryl sulfate (SLS); cocamidopropyl betaine (CAPB); and Tergitol™15-S-9, may also affect the degree of hydrophobicity imparted to the surface. The hydrophobicity may be reduced; however this may be advantageous in certain applications, for instance in allowing better penetration of water soluble actives such as fluoride onto the tooth surface while still providing sufficient surface protection.

An increase in the concentration of the organophosphate will generally provide increased hydrophobicity of the tooth surface with a corresponding increase in surface protection against acid attack. The data in Table 2 above demonstrate an increase in hydrophobic modification of
tooth surface with increased in concentration of sodium dodeceth-1 phosphate and a corresponding
increase in protection of the surface against acid attack.

Table 3: Surface Hydrophobic Effects of Organophosphate Compounds in the Presence of Water Soluble Hydrophilic Compounds

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Δ Water Contact Angle</th>
<th>% Inhibition of HAP Surface Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0% Sodium Dodeceth-1 Phosphate</td>
<td>32.13</td>
<td>94.49</td>
</tr>
<tr>
<td>1% Sodium acid pyrophosphate</td>
<td>1.07</td>
<td>34.26</td>
</tr>
<tr>
<td>1% Sodium Dodeceth-1 Phosphate + 1% Sodium acid pyrophosphate</td>
<td>35.73</td>
<td>71.71</td>
</tr>
</tbody>
</table>

The data in Table 3 above demonstrate that organophosphates retain their hydrophobic surface modification properties even when used in combination with hydrophilic oral care agents such as pyrophosphate that tend to make the surface hydrophilic when used alone. Other such hydrophilic agents include water soluble phosphorylated compounds such as triplyphosphate and longer chain polyphosphates (n≥4) or polycarboxylates such as polyacrylates and the copolymer of maleic anhydride or acid and methyl vinyl ether (available as Gantrez®). The compatibility of organophosphates with pyrophosphate enables formulation of these ingredients together in toothpaste compositions. Importantly the present toothpaste compositions with pyrophosphate are found to have improved soft tissue tolerance to pyrophosphate, a commonly used tartar control ingredient. A number of consumers have reported sensitivity to pyrophosphate toothpastes manifested by sloughing off thin mucosal lining or desquamation during the normal brushing process. It is believed the control of desquamation is yet another benefit derived from the hydrophobic coating of oral cavity surfaces.

Further in a consumer perception study, panelists rated a toothpaste formulation containing an organophosphate and pyrophosphate (Example I-E below) as replenishing enamel’s shine and improving the shine of teeth significantly better than an ordinary toothpaste, using a 5-point scale (Excellent – Very Good – Good – Fair – Poor). In this study, each panelist evaluated the shine on their teeth after brushing with each of a test product containing an organophosphate and a control product (Crest® Cavity Protection) on 2 sequential days. For each brushing, panelists used ADA manual reference (40 soft) brush. Panelists dispensed product themselves and brushed as they normally do, waited 10 minutes and performed the shine evaluation on their teeth. Shine evaluation was conducted using a mirror in a sink lab with inside fluorescent bulbs (GE Ecolux with Starcoat F17T8 SP30 ECO 17W) on and overhead lights off.
Mirrors can be pulled all the way forward on the tracks and panelists can adjust from there as necessary for their evaluation.

Tables 4 and 5. Hydrophobic Surface Modification of Tooth Surface Using Hydrophobic Compounds Alone and in Combination with Organophosphate

<table>
<thead>
<tr>
<th>(4) Treatment</th>
<th>Δ Water Contact Angle</th>
<th>Enamel Surface Loss µ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petrolatum</td>
<td>53.27</td>
<td>9.0</td>
</tr>
<tr>
<td>Versagel™*</td>
<td>54.80</td>
<td>16.5</td>
</tr>
<tr>
<td>Microcrystalline Wax</td>
<td>-</td>
<td>2.88</td>
</tr>
<tr>
<td>Fluoride paste</td>
<td>0</td>
<td>23.5</td>
</tr>
</tbody>
</table>

* Versagel™ is gelled hydrogenated polyisobutene supplied by Penreco.

<table>
<thead>
<tr>
<th>(5) Treatment</th>
<th>Δ Water Contact Angle After Treatment</th>
<th>Δ Water Contact Angle After Water Brushing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petrolatum (Ex. III-B)</td>
<td>20.7</td>
<td>0</td>
</tr>
<tr>
<td>Petrolatum + Potassium dodecyl phosphate (Ex. III-D)</td>
<td>44.1</td>
<td>21.2</td>
</tr>
<tr>
<td>Mineral oil + Potassium Laureth phosphate (Ex.III-F)</td>
<td>18.7</td>
<td>19.5</td>
</tr>
<tr>
<td>Cetyl alcohol / Stearyl alcohol (Ex. I-H)</td>
<td>5.1</td>
<td>-</td>
</tr>
<tr>
<td>Cetyl alcohol / Stearyl alcohol + dodecyl phosphate (Ex.I-G)</td>
<td>19.0</td>
<td>-</td>
</tr>
</tbody>
</table>

Data in Tables 4 and 5 above show changes in water contact angle of the tooth surface after treatment with hydrophobic compounds used alone or in combination with an organophosphate. The hydrophobic compounds applied directly to the tooth surface provided hydrophobic modification and better protection in terms of less mineral surface loss after acid challenge compared to a regular fluoride toothpaste treatment (Crest® Cavity Protection toothpaste from Procter & Gamble). Testing of various formulations illustrated in the Examples below demonstrate that organophosphates serve as a carrier for other hydrophobic materials. The combination provides increased and longer lasting hydrophobicity of the surface, as demonstrated by retention of increased contact angle even after brushing.

Orally Acceptable Carriers

The compositions may comprise optional components (collectively referred to as orally acceptable carriers or excipients) which are described in the following paragraphs along with non-limiting examples. These orally acceptable carrier materials include one or more compatible solid or liquid excipients or diluents which are suitable for topical oral administration. By “compatible” is meant that the components of the composition are capable of being commingled without interaction in a manner which would substantially reduce composition stability and/or
efficacy. Suitable carriers or excipients are well known in the art. Their selection will depend on secondary considerations like taste, cost, and shelf stability, etc.

Fluoride Source

A fluoride ion source is typically present in dentifrices and other oral compositions in amounts sufficient to give a fluoride ion concentration in the composition to provide anticaries effectiveness. The fluoride ion source will typically comprise from about 0.0025% to about 5.0% or from about 0.005% to about 2.0% by weight of the composition. As discussed above, prevention of caries is essential for overall tooth health and integrity. A wide variety of fluoride ion-yielding materials can be employed as sources of soluble fluoride. Representative fluoride ion sources include: stannous fluoride, sodium fluoride, potassium fluoride, amine fluoride, sodium monofluorophosphate, indium fluoride and many others.

In commonly assigned application published as US 2008/0247973A1, it is reported that alkyl phosphates can influence fluoride uptake. Alkyl phosphates which make surfaces relatively more hydrophobic provide good surface protection but relatively less fluoride uptake than alkyl phosphates that make surfaces less hydrophobic, such as alkyl phosphates that either have ethoxy groups or large polar counter ions that make them relatively more hydrophilic. Generally, the relatively more hydrophilic organophosphates allow good fluoride uptake and provide acceptable surface protection benefits. Thus formulating compositions comprising organophosphates and fluoride may require careful selection of organophosphate species and/or adjusting the formulation in order to ensure that both anti-caries efficacy from fluoride and surface protection benefits from the organophosphate are delivered.

In one embodiment, a dentifrice product within a single container comprises two thermodynamically stable but separate phases, the first phase comprising a fluoride ion source in an aqueous carrier and the second phase comprising an organophosphate compound in a non-aqueous carrier, wherein the fluoride phase is delivered before the organophosphate phase such that teeth become exposed to fluoride prior to exposure to the organophosphate. The fluoride phase being an aqueous phase would solubilize in the mouth faster than a non-aqueous organophosphate phase.

In another embodiment, a dentifrice product comprises at least two separate phases contained in separate compartments of a dispenser. One compartment contains a fluoride phase and another compartment contains an organophosphate phase. The dual-phase composition provides a means to allow fluoride deposition on the teeth prior to deposition of the organophosphate. In a single phase embodiment containing fluoride and organophosphate
together, delayed release of the organophosphate can be accomplished for example, by encapsulating the organophosphate and triggering release of the organophosphate by a pH change, mechanical shear, dilution or other mechanism.

Antimicrobial Agent

The present compositions may include an antimicrobial agent, such as a quaternary ammonium antimicrobial agent to provide bactericidal efficacy, i.e., effectiveness in killing, and/or altering metabolism, and/or suppressing the growth of, microorganisms which cause topically-treatable infections and diseases of the oral cavity, such as plaque, caries, gingivitis, and periodontal disease.

The antimicrobial quaternary ammonium compounds used in the compositions of the present invention include those in which one or two of the substitutes on the quaternary nitrogen has a carbon chain length (typically alkyl group) from about 8 to about 20, typically from about 10 to about 18 carbon atoms while the remaining substitutes (typically alkyl or benzyl group) have a lower number of carbon atoms, such as from about 1 to about 7 carbon atoms, e.g., methyl or ethyl groups. Dodecyl trimethyl ammonium bromide, domiphen bromide, cetylpyridinium chloride (CPC), tetradecylpyridinium chloride, N-tetradecyl-4-ethyl pyridinium chloride, dodecyl dimethyl (2-phenoxethyl) ammonium bromide, benzyl dimethylolesteram ammonium chloride, quaternized 5-amino-1,3-bis(2-ethyl-hexyl)-5-methyl hexahydropyrimidine, benzalkonium chloride, benzethonium chloride, methyl benzethonium chloride and bis[4-(R-amino)-1-pyridinium] alkanes are exemplary of typical quaternary ammonium antimicrobial agents. Commonly used pyridinium compounds include cetylpyridinium, or tetradecylpyridinium halide salts (i.e., chloride, bromide, fluoride and iodide). The quaternary ammonium antimicrobial agents may be included in the present compositions at levels of at least about 0.035%, typically from about 0.045% to about 1.0% or from about 0.05% to about 0.10% by weight.

As described in commonly assigned application WO 05/072693, the bioavailability and activity of quaternary ammonium antimicrobials are negatively affected particularly by anionic surfactants, which are common ingredients in oral care formulations. Thus, it is particularly surprising that some of the present surface-active and anionic organophosphate compounds would be compatible with quaternary ammonium antimicrobials such as CPC, in that the bioavailability and antimicrobial activity are not significantly affected.

The present compositions may comprise a metal ion source that provides stannous ions, zinc ions, copper ions, or mixtures thereof as antimicrobial agent. The metal ion source can be a soluble or a sparingly soluble compound of stannous, zinc, or copper with inorganic or organic
counter ions. Examples include the fluoride, chloride, chlorofluoride, acetate, hexafluorozirconate, sulfate, tartrate, gluconate, citrate, malate, glycinate, pyrophosphate, metaphosphate, oxalate, phosphate, carbonate salts and oxides of stannous, zinc, and copper.

Stannous, zinc and copper ions have been found effective to reduce gingivitis, plaque, and sensitivity and provide improved breath benefits. An effective amount is defined as from about 50 ppm to about 20,000 ppm metal ion of the total composition or from about 500 ppm to about 15,000 ppm. Typically, metal ions are present in an amount from about 3,000 ppm to about 13,000 ppm or from about 5,000 ppm to about 10,000 ppm. This is the total amount of metal ions (stannous, zinc, copper and mixtures thereof) for delivery to the tooth surface.

Stannous salts including stannous fluoride and stannous chloride typically used in dentifrices, are described in e.g., U.S. Patent Nos. 5,004,597 to Majeti et al.; 5,578,293 to Prencipe et al. and 5,281,410 to Lukacovic et al. Other suitable stannous salts include stannous acetate, stannous tartrate and sodium stannous citrate. Examples of suitable zinc ion sources are zinc oxide, zinc sulfate, zinc chloride, zinc citrate, zinc lactate, zinc gluconate, zinc malate, zinc tartrate, zinc carbonate, zinc phosphate, and other salts listed in U.S. Pat. No 4,022,880. Zinc citrate and zinc lactate are commonly used. Examples of suitable copper ion sources are listed in U.S. Pat. No. 5,534,243. The combined metal ion source(s) may be present in an amount of from about 0.05% to about 11%, by weight of the final composition, from about 0.5 to about 7%, or from about 1% to about 5%. The stannous salts may be present in an amount of from about 0.1 to about 7%, from about 1% to about 5%, or from about 1.5% to about 3% by weight of the total composition. The amount of zinc or copper salts used in the present invention may range from about 0.01 to about 5%, from about 0.05 to about 4%, or from about 0.1 to about 3.0%.

Other antimicrobial agents useful herein include non-cationic antimicrobial agents such as halogenated diphenyl ethers, phenolic compounds including phenol and its homologs, mono and poly-alkyl and aromatic halophenols, resorcinol and its derivatives, xylitol, bisphenolic compounds and halogenated salicylanilides, benzoic esters, and halogenated carbanilides. Also useful as antimicrobials are enzymes, including endoglycosidase, papain, dextranase, mutanase, and mixtures thereof. Commonly used antimicrobial agents include chlorhexidine, triclosan, triclosan monophosphate, and essential oils such as thymol. These agents may be present at levels of from about 0.01% to about 1.5%, by weight of the composition.

Anticalculus Agent

The present compositions may optionally include an anticalculus agent, such pyrophosphate ions provided by pyrophosphate salts such as mono-, di- and tetraalkali metal
pyrophosphates. Disodium dihydrogen pyrophosphate (Na₂H₂P₂O₇), sodium acid pyrophosphate, tetraboron pyrophosphate (Na₄P₂O₇), and tetraborate pyrophosphate (K₂P₂O₇) in their unhydrated or hydrated forms are commonly used species. The pyrophosphate salt may be present as predominately dissolved, predominately undissolved, or a mixture of dissolved and undissolved pyrophosphate. In some embodiments the amount of free pyrophosphate ions may be from about 1% to about 15%, from about 1.5% to about 10% or from about 2% to about 6%. Free pyrophosphate ions may be present in a variety of protonated states depending on the pH of the composition.

Compositions comprising predominately undissolved pyrophosphate refer to compositions containing no more than about 20% of the total pyrophosphate salt dissolved in the composition, typically less than about 10% of the total pyrophosphate dissolved in the composition. Tetrasodium pyrophosphate salt is a typical pyrophosphate salt in these compositions, in anhydrous salt form, the dehydrate form, or any other species stable in solid form in the dentifrice compositions. The salt is in its solid particle form, which may be its crystalline and/or amorphous state, with the particle size of the salt preferably being small enough to be aesthetically acceptable and readily soluble during use. The amount of pyrophosphate salt useful in making these compositions is any tartar control effective amount, generally from about 1.5% to about 15%, from about 2% to about 10%, or from about 3% to about 8%, by weight.

Optional agents to be used in place of or in combination with the pyrophosphate salt include such known materials as longer chain polyphosphates (n=3 or more) including tripolyphosphate, tetrapolyphosphate and hexametaphosphate; synthetic anionic polymers, including polyacrylates and copolymers of maleic anhydride or acid and methyl vinyl ether (e.g., Grenz®), as well as, e.g., polyamino prostate sulfonic acid (AMPS), diphosphonates (e.g., EHDP, AHP), polypeptides (such as polyaspartic and polyglycamic acids), and mixtures thereof.

Other Active Agents

Another active agent that may be included in the present compositions is a tooth bleaching active selected from peroxides, perborates, percarbonates, peroxyacids, persulfates, and combinations thereof. Suitable peroxide compounds include hydrogen peroxide, urea peroxide, calcium peroxide, sodium peroxide, zinc peroxide and mixtures thereof. A commonly used percarbonate is sodium percarbonate. A common persulfate is potassium peroxymonosulfate (also known as MPS and the trade names Caroat and Oxone).

Commonly used peroxide sources in dentifrice formulations include calcium peroxide and urea peroxide. Hydrogen peroxide and urea peroxide are typically used in mouthrinse
formulations. The present composition may contain from about 0.01% to about 30%, from about
0.1% to about 10%, or from about 0.5% to about 5% of a peroxide source, by weight.

In addition to whitening, the peroxide also provides other benefits to the oral cavity,
including curative and/or prophylactic treatment of caries, dental plaque, gingivitis, periodontitis,
mouth odor, recurrent aphthous ulcers, denture irritations, orthodontic appliance lesions, post-
extraction and post-periodontal surgery, traumatic oral lesions and mucosal infections, herpetic
stomatitis and the like.

Another optional active agent that may be added to the present compositions is a dentinal
desensitizing agent to control hypersensitivity, such as salts of potassium, calcium, strontium and
tin including nitrate, chloride, fluoride, phosphates, pyrophosphate, polyphosphate, citrate,
oxalate and sulfate.

The present compositions may optionally include nutrients particularly those that improve
the condition of the oral cavity, such as minerals, vitamins, and amino acids. Amino acids useful
in the composition of the invention include basic amino acids such as arginine, lysine, histidine,
their salts and/or combinations thereof. Examples of minerals include calcium, phosphorus,
fluoride, zinc, manganese, potassium and mixtures thereof. In particular calcium salts may be
included in the present compositions to provide mineralization and tooth strengthening benefits.

Once deposited on the tooth surface, the organophosphate coating would prevent these
active agents from being rapidly washed away.

Tooth Substantive Agent

The present invention may include a tooth substantive agent such as polymeric surface
active agents (PMSA’s), which are polyelectrolytes, for example, anionic polymers, provided
they do not significantly affect the desired hydrophobic modification herein. The PMSA’s
contain anionic groups, e.g., phosphate, phosphonate, carboxy, or mixtures thereof, and thus,
have the capability to interact with cationic or positively charged entities. The “mineral”
descriptor is intended to convey that the surface activity or substantivity of the polymer is toward
mineral surfaces such as calcium phosphate minerals in teeth.

PMSA’s are useful in the present compositions because of their stain prevention benefit. It is believed the PMSA’s provide a stain prevention benefit because of their reactivity or
substantivity to mineral surfaces, resulting in desorption of portions of undesirable adsorbed
pellicle proteins, in particular those associated with binding color bodies that stain teeth, calculus
development and attraction of undesirable microbial species. The retention of these PMSA’s on
teeth can also prevent stains from accruing due to disruption of binding sites of color bodies on tooth surfaces.

The ability of PMSA’s to bind stain promoting ingredients of oral care products, for example, stannous ions and cationic antimicrobials, is also believed to be helpful. The PMSA will also provide tooth surface conditioning effects which produce desirable effects on surface thermodynamic properties and surface film properties, which impart improved clean feel aesthetics both during and most importantly, following rinsing or brushing. Many of these polymeric agents are also known or expected to provide tartar control benefits when applied in oral compositions, hence providing improvement in both the appearance of teeth and their tactile impression to consumers.

Suitable examples of PMSA’s are polyelectrolytes such as condensed phosphorylated polymers; polyphosphonates; copolymers of phosphate- or phosphonate-containing monomers or polymers with other monomers such as ethylenically unsaturated monomers and amino acids or with other polymers such as proteins, polypeptides, polysaccharides, poly(acrylate), poly(acrylamide), poly(methacrylate), poly(ethylacrylate), poly(hydroxyalkylmethacrylate), poly(vinyl alcohol), poly(maleic anhydride), poly(maleate) poly(amide), poly(ethylene amine), poly(ethylene glycol), poly(propylene glycol), poly(vinyl acetate) and poly(vinyl benzyl chloride); polycarboxylates and carboxy-substituted polymers; and mixtures thereof. Suitable polymeric mineral surface active agents include the carboxy-substituted alcohol polymers described in U.S. Patent Nos. 5,292,501; 5,213,789; 5,093,170; 5,009,882; and 4,939,284; all to Degenhardt et al. and the diphosphonate-derivatized polymers in U.S. Patent 5,011,913 to Benedict et al.; the synthetic anionic polymers including polyacrylates and copolymers of maleic anhydride or acid and methyl vinyl ether (e.g., Gantrez®), as described, for example, in U.S. Patent 4,627,977; to Gaffar et al. Diphosphonate modified polyacrylic acid is one example.

Polymers with activity must have sufficient surface binding propensity to desorb pellicle proteins and remain affixed to enamel surfaces. For binding to tooth surfaces, polymers with end or side chain phosphate or phosphonate functions are effective although other polymers with mineral binding activity may also be effective depending upon adsorption affinity.

Additional examples of suitable phosphonate containing polymeric mineral surface active agents include the geminal diphosphonate polymers disclosed as anticalculus agents in US 4,877,603 to Degenhardt et al.; phosphonate group containing copolymers disclosed in US 4,749,758 to Dursch et al. and in GB 1,290,724 (both assigned to Hoechst) suitable for use in detergent and cleaning compositions; and the copolymers and cotelomers disclosed as useful for
applications including scale and corrosion inhibition, coatings, cements and ion-exchange resins in US 5,980,776 to Zakikhani et al. and US 6,071,434 to Davis et al. Additional polymers include the water-soluble copolymers of vinylphosphonic acid and acrylic acid and salts thereof disclosed in GB 1,290,724 wherein the copolymers contain from about 10% to about 90% by weight vinylphosphonic acid and from about 90% to about 10% by weight acrylic acid, more particularly wherein the copolymers have a weight ratio of vinylphosphonic acid to acrylic acid of 70% vinylphosphonic acid to 30% acrylic acid; 50% vinylphosphonic acid to 50% acrylic acid; or 30% vinylphosphonic acid to 70% acrylic acid. Other suitable polymers include the water soluble polymers disclosed by Zakikhani and Davis prepared by copolymerizing diphosphonate or polyphosphonate monomers having one or more unsaturated C= C bonds (e.g., vinylidene-1,1-diphosphonic acid and 2-(hydroxyphosphinyl)ethylidene-1,1-diphosphonic acid), with at least one further compound having unsaturated C= C bonds (e.g., acrylate and methacrylate monomers). Examples of suitable polymers include the diphosphonate/acrylate polymers supplied by Rhodia under the designation ITC 1087 (Average MW 3000-60,000) and Polymer 1154 (Average MW 6000-55,000).

Among useful PMSA’s herein are polyphosphates. A polyphosphate is generally understood to consist of two or more phosphate molecules arranged primarily in a linear configuration, although some cyclic derivatives may be present. Although pyrophosphates (n=2) are technically polyphosphates, particularly useful polyphosphates as PMSA are those having around three or more phosphate groups so that surface adsorption at effective concentrations produces sufficient non-bound phosphate functions, which may enhance the anionic surface charge and affect the hydrophilicity of the surfaces. Examples of inorganic polyphosphate salts include tripolyphosphate, tetrapolyposphate and hexametaphosphate, among others. The linear polyphosphates are represented by the formula: XO(XPO3)nxX, wherein X is typically sodium, potassium or ammonium and n averages from about 3 to about 125. Commercially available longer-chain polyphosphates having n averaging from about 6 to about 21 include those known as Sodaphos (n=6), Hexaphos (n=13), and Glass H (n=21) and are supplied by FMC Corporation and Astaris. Polyphosphates are susceptible to hydrolysis in high water formulations at acid pH, particularly below pH 5. Thus longer-chain polyphosphates are particularly useful, such as Glass H. It is believed longer-chain polyphosphates when undergoing hydrolysis produce shorter-chain polyphosphates which are still effective to deposit onto teeth and provide a stain preventive benefit.
Other polyphosphorylated compounds may be used in addition to or instead of the polyphosphate, in particular polyphosphorylated inositol compounds such as phytic acid also known as myo-inositol 1,2,3,4,5,6-hexakis (dihydrogen phosphate) or inositol hexaphosphoric acid; myo-inositol pentakis(dihydrogen phosphate); myo-inositol tetrakis(dihydrogen phosphate), myo-inositol tris(dihydrogen phosphate), and an alkali metal, alkaline earth metal or ammonium salt thereof. Herein, the term “phytate” includes phytic acid and its salts as well as other polyphosphorylated inositol compounds.

The amount of tooth substantive agent may range from about 0.1% to about 35% by weight of the total oral composition. In dentifrice formulations, the amount is typically from about 2% to about 30%, from about 5% to about 25%, or from about 6% to about 20%. In mouthrinse compositions, the amount of tooth substantive agent may range from about 0.1% to 5% or from about 0.5% to about 3%.

In addition to creating the surface modifying effects, the tooth substantive agent may also function to solubilize insoluble salts. For example, Glass H has been found to solubilize insoluble stannous salts. Thus, in compositions containing stannous fluoride for example, Glass H contributes to decreasing the stain promoting effect of stannous.

Chelating agents

Another optional agent is a chelating agent, also called sequestrants, such as gluconic acid, tartaric acid, citric acid and pharmaceutically-acceptable salts thereof. Chelating agents are able to complex calcium found in the cell walls of the bacteria. Chelating agents can also disrupt plaque by removing calcium from the calcium bridges which help hold this biomass intact. However, it is not desired to use a chelating agent which has an affinity for calcium that is too high, as this may result in tooth demineralization, which is contrary to the objects and intentions of the present invention. Suitable chelating agents will generally have a calcium binding constant of about $10^1$ to $10^5$ to provide improved cleaning with reduced plaque and calculus formation. Chelating agents also have the ability to complex with metallic ions and thus aid in preventing their adverse effects on the stability or appearance of products. Chelation of ions, such as iron or copper, helps retard oxidative deterioration of finished products.

Examples of suitable chelating agents are sodium or potassium gluconate and citrate; citric acid/alkali metal citrate combination; disodium tartrate; dipotassium tartrate; sodium potassium tartrate; sodium hydrogen tartrate; potassium hydrogen tartrate; sodium, potassium or ammonium polyphosphates and mixtures thereof. The chelating agent may be used from about 0.1% to about 2.5%, from about 0.5% to about 2.5% or from about 1.0% to about 2.5%.
Still other chelating agents suitable for use in the present invention are the anionic polymeric polycarboxylates. Such materials are well known in the art, being employed in the form of their free acids or partially or fully neutralized water soluble alkali metal (e.g., potassium and sodium) or ammonium salts. Examples are 1:4 to 4:1 copolymers of maleic anhydride or acid with another polymerizable ethylenically unsaturated monomer, such as methyl vinyl ether (methoxyethylene) having a molecular weight (M.W.) of about 30,000 to about 1,000,000. These copolymers are available for example as Gantrez AN 139 (M.W. 500,000), AN 119 (M.W. 250,000) and S-97 Pharmaceutical Grade (M.W. 70,000), of GAF Chemicals Corporation.

Other operative polymeric polycarboxylates include the 1:1 copolymers of maleic anhydride with ethyl acrylate, hydroxyethyl methacrylate, N-vinyl-2-pyrrolidone, or ethylene, the latter being available for example as Monsanto EMA No. 1103, M.W. 10,000 and EMA Grade 61, and 1:1 copolymers of acrylic acid with methyl or hydroxyethyl methacrylate, methyl or ethyl acrylate, isobutyl vinyl ether or N-vinyl-2-pyrrolidone. Additional operative polymeric polycarboxylates include copolymers of maleic anhydride with styrene, isobutylene or ethyl vinyl ether; polyacrylic, polyitaconic and polymaleic acids; and sulfaoacrylic oligomers of MW as low as 1,000 available as Uniroyal ND-2.

Surfactants

The present compositions will typically also comprise surfactants, also commonly referred to as sudsing agents. Suitable surfactants are those which are reasonably stable and foam throughout a wide pH range. The surfactant may be anionic, nonionic, amphoteric, zwitterionic, cationic, or mixtures thereof. Preferred surfactants or surfactant mixtures are those that are compatible with the organophosphate agent and other actives in the composition in that the activities of these components are not compromised. Anionic surfactants, such as sodium alkyl sulfate, amphoteric surfactants, such as cocoamidopropyl betaine and their mixtures are typical examples.

Anionic surfactants useful herein include the water-soluble salts of alkyl sulfates having from 8 to 20 carbon atoms in the alkyl radical (e.g., sodium alkyl sulfate) and the water-soluble salts of sulfonated monoglycerides of fatty acids having from 8 to 20 carbon atoms. Sodium lauryl sulfate (SLS) and sodium coconut monoglyceride sulfonates are examples of anionic surfactants of this type. Other suitable anionic surfactants include sarcosinates, isethionates and taurotes. Examples for use herein include alkali metal or ammonium salts of these surfactants, such as the sodium and potassium salts of the following: lauroyl sarcosinate, myristoyl sarcosinate, palmitoyl sarcosinate, stearoyl sarcosinate, oleoyl sarcosinate and lauroyl.
isethionate. Other examples of anionic surfactants are sodium lauryl sulfoacetate, sodium, sodium laureth carboxylate, and sodium dodecyl benzenesulfonate. The composition will typically comprise one or a mixture of anionic surfactants at a level of from about 0.025% to about 9%, from about 0.05% to about 5% or from about 0.1% to about 1%.

Zwitterionic or amphoteric surfactants useful in the present invention include derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight chain or branched, and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate or phosphonate. Suitable betaine surfactants include decyl betaine or 2-(N-decyl-N,N-dimethylammonio)acetate, coco betaine or 2-(N-coco-N, N-dimethyl ammonio)acetate, myristyl betaine, palmityl betaine, lauryl betaine, cetyl betaine, cetyl betaine, stearyl betaine, etc. The amidobetaines are exemplified by cocoamidoethyl betaine, cocamidopropyl betaine (CAPB), and lauramidopropyl betaine.

Cationic surfactants useful in the present invention include derivatives of quaternary ammonium compounds having one long alkyl chain containing from about 8 to 18 carbon atoms such as lauryl trimethylammonium chloride; cetyl pyridinium chloride; cetyl trimethylammonium bromide; coconut alkyltrimethylammonium nitrate; cetyl pyridinium fluoride; etc. Certain cationic surfactants can also function as antimicrobials herein.

Nonionic surfactants include compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound which may be aliphatic or alkylaromatic in nature. Examples of suitable nonionic surfactants include the Pluronics, polyethylene oxide condensates of alkyl phenols, products derived from the condensation of ethylene oxide with the reaction product of propylene oxide and ethylene diamine, ethylene oxide condensates of aliphatic alcohols, long chain tertiary amine oxides, long chain tertiary phosphine oxides, long chain dialkyl sulfoxides and mixtures of such materials.

Abrasives

Dental abrasives may optionally be included in the compositions of the subject invention. Some compositions contemplated herein such as dental gels and finishing gels will preferably be abrasive-free. When present, the abrasive material selected must be one which is compatible with the other components of the composition and will not excessively abrade dentin. Suitable abrasives include, for example, silicas including gels and precipitates, insoluble sodium polymetaphosphate, hydrated alumina, calcium carbonate, dicalcium orthophosphate dihydrate, calcium pyrophosphate, tricalcium phosphate, calcium polymetaphosphate, and resinous abrasive
materials such as particulate condensation products of urea and formaldehyde, cross-linked epoxides, and cross-linked polyesters.

Silica dental abrasives of various types are particularly useful because of their unique benefits of exceptional dental cleaning and polishing performance without unduly abrading tooth enamel or dentine. The silica abrasive polishing materials herein, as well as other abrasives, may have an average particle size ranging between about 0.1 to about 30 microns, typically from about 3 to about 20 microns. The abrasive can be precipitated silica or silica gels such as the silica xerogels. Examples include the silica xerogels marketed under the trade name "Syloid" by the W.R. Grace & Company and precipitated silica materials such as those marketed by the J. M. Huber Corporation under the trade name, Zeodent®, particularly the silicas carrying the designation Zeodent® 119, Zeodent® 118, Zeodent® 109 and Zeodent® 129. Mixtures of abrasives can be used such as mixtures of the various grades of Zeodent® silica abrasives listed above. The total amount of abrasive in dentifrice compositions of the subject invention may range from about 6% to about 70% by weight; toothpastes typically contain from about 10% to about 50% of abrasives. Dental solution, mouth spray, mouthwash and non-abrasive gel compositions of the subject invention typically contain little or no abrasive.

Flavor System

The flavor system is typically added to oral care compositions, to provide a pleasant tasting composition and to effectively mask any unpleasant taste and sensations due to certain components of the composition such as antimicrobial actives or peroxide. Pleasant tasting compositions improve user compliance to prescribed or recommended use of oral care products. The present flavor system will comprise flavor components, in particular those that have been found to be relatively stable in the presence of usual oral care product actives and carriers.

Non-limiting examples of flavor components include flavorants such as peppermint oil, corn mint oil, spearmint oil, oil of wintergreen, clove bud oil, cassia, sage, parsley oil, marjoram, lemon, lime, orange, cis-jasmone, 2,5-dimethyl-4-hydroxy-3(2H)-furanone, 5-ethyl-3-hydroxy-4-methyl-2(5H)-furanone, vanillin, ethyl vanillin, anisaldehyde, 3,4-methylenedioxybenzaldehyde, 3,4-dimethoxybenzaldehyde, 4-hydroxybenzaldehyde, 2-methoxybenzaldehyde, benzaldehyde; cinnamaldehyde, hexyl cinnamaldehyde, alpha-methyl cinnamaldehyde, ortho-methoxy cinnamaldehyde, alpha-amy1 cinnamaldehydepropenyl guaethol, heliotropine, 4-cis-heptenal, diacetyl, methyl-p-tert-butyl phenyl acetate, menthol, methyl salicylate, ethyl salicylate, 1-menthol acetate, oxanone, alpha-irisone, methyl cinnamate, ethyl cinnamate, butyl cinnamate, ethyl butyrate, ethyl acetate, methyl anthranilate, iso-amyl acetate, iso-amyl butyrate, allyl
caproate, eugenol, eucalyptol, thymol, cinnamic alcohol, octanol, octanal, decanol, decanal, phenylethyl alcohol, benzyl alcohol, alpha-terpineol, linalool, limonene, citral, maltol, ethyl maltol, anethole, dihydroanethole, carvone, menthone, β-damascenone, ionone, gamma decalactone, gamma nonalactone, gamma undecalactone and mixtures thereof. Generally suitable flavorants are those containing structural features and functional groups that are less prone to redox reactions. Flavor agents or flavorants are generally used in the compositions at levels of from about 0.001% to about 5%, by weight of the composition.

The flavor system will typically include a sweetening agent. Suitable natural water-soluble sweeteners include monosaccharides, disaccharides and polysaccharides such as xylose, ribose, glucose (dextrose), mannose, galactose, fructose (levulose), sucrose (sugar), maltose, invert sugar (a mixture of fructose and glucose derived from sucrose), partially hydrolyzed starch, corn syrup solids, dihydrochalcones, monellin, steviosides, and glycyrrhizin. Suitable water-soluble artificial sweeteners include soluble saccharin salts, i.e., sodium or calcium saccharin salts, cyclamate salts, the sodium, ammonium or calcium salt of 3,4-dihydro-6-methyl-1,2,3-oxathiazine-4-one-2,2-dioxide, the potassium salt of 3,4-dihydro-6-methyl-1,2,3-oxathiazine-4-one-2,2-dioxide (acesulfame-K), the free acid form of saccharin, and the like. Other suitable sweeteners include dipeptide based sweeteners, such as L-aspartic acid derived sweeteners, including L-aspartyl-L-phenylalanine methyl ester (aspartame) L-alpha-aspartyl-N-(2,2,4,4-tetramethyl-3-thietanyl)-D-alaninamide hydrate, methyl esters of L-aspartyl-L-phenylglycerin and L-aspartyl-L-2,5-dihydrophenyl-glycine, L-aspartyl-2,5-dihydro-L-phenylalanine, L-aspartyl-L-(1-cyclohexyl)-alanine, and the like. Water-soluble sweeteners derived from naturally occurring water-soluble sweeteners, such as a chlorinated derivative of ordinary sugar (sucrose), known under the product description of sucralose and protein based sweeteners such as thaumatococcus danielli (Thaumatin I and II) may be used. Compositions typically contain from about 0.1% to about 10% of sweetener.

Suitable cooling agents or coolants for use in the flavor system include a wide variety of materials such as menthol and its derivatives. Many synthetic coolants are derivatives of or are structurally related to menthol, i.e., containing the cyclohexane moiety, and derivatized with functional groups including carboxamide, ketal, ester, ether and alcohol. Examples include the ρ-menthanecarboxamide compounds such as N-ethyl-ρ-menthan-3-carboxamide, known commercially as "WS-3", and others in the series such as WS-5, WS-12 and WS-14. Examples of menthane carboxy esters include WS-4 and WS-30. An example of a synthetic carboxamide coolant that is structurally unrelated to menthol is N,2,3-trimethyl-2-isopropylbutanimide,
known as “WS-23”. Additional suitable coolants include 3-1-methoxypropane-1,2-diol known as TK-10, isopulegol (under the tradename Coolact P) and ρ-methane-3,8-diol (under the tradename Coolact 38D) all available from Takasago; menthone glycerol acetal known as MGA; menthyl esters such as menthyl acetate, menthyl acetoacetate, menthyl lactate known as Frescolat® supplied by Haarmann and Reimer, and monomenthyl succinate under the tradename Physcool from V. Mane. Additional useful N-substituted ρ-methane carboxamides are described as having high cooling potency and long lasting sensory effect in WO 2005/049553A1 and include for example, N-(4-cyanomethylphenyl)-ρ-methanecarboxamide, supplied by Givaudan under the designation G-180 coolant.

The flavor system may also include salivating agents, hydration and moisturization agents, and other sensates such as warming agents and numbing agents. These agents are present in the compositions at a level of from about 0.001% to about 10% or from about 0.1% to about 1%. Suitable salivating agents include Jambu® supplied by Takasago and Optaflow® from Symrise. Hydration agents include polyols such as erythritol. Suitable numbing agents include benzocaine, lidocaine, clove bud oil, and ethanol. Warming agents include ethanol, capsicum and nicotine esters, such as benzyl nicotinate.

Miscellaneous Carrier Materials

Water employed in the preparation of commercially suitable oral compositions should preferably be of low ion content and free of organic impurities. Water may comprise up to about 99% by weight of the aqueous compositions herein. These amounts of water include the free water which is added plus that which is introduced with other materials, such as with sorbitol.

The present compositions in the form of toothpastes, dentifrices and gels typically will contain some thickening material or binder to provide a desirable consistency. Typical thickening agents include carboxyvinyl polymers, carrageenan, hydroxyethyl cellulose, and water soluble salts of cellulose ethers such as sodium carboxymethylcellulose and sodium hydroxyethyl cellulose. Natural gums such as gum karaya, xanthan gum, gum arabic, and gum tragacanth can also be used. Colloidal magnesium aluminum silicate or finely divided silica can be used as part of the thickening agent to further improve texture. Thickening agents are typically used in an amount from about 0.1% to about 15%, by weight.

The present compositions may also include an alkali metal bicarbonate salt, which may serve a number of functions including abrasive, deodorant, buffering and adjusting pH. Sodium bicarbonate, also known as baking soda, is commonly used. The present composition may contain from about 0.5% to about 30% by weight of an alkali metal bicarbonate salt.
The pH of the present compositions may be adjusted through the use of buffering agents. For example, buffering agents are used to adjust the pH of aqueous compositions such as mouthrinses and dental solutions typically to a range of about pH 4.0 to about pH 8.0. Buffering agents include sodium bicarbonate, monosodium phosphate, trisodium phosphate, sodium hydroxide, sodium carbonate, sodium acid pyrophosphate, citric acid and sodium citrate and may be included at a level of from about 0.5% to about 10% by weight.

Titanium dioxide may also be added to the present compositions as coloring or opacifying agent typically at a level of from about 0.25% to about 5% by weight.

Poloxamers may be employed in the present compositions. A poloxamer is classified as a nonionic surfactant and may also function as an emulsifying agent, binder, stabilizer, and other related functions. Poloxamers are difunctional block-polymers terminating in primary hydroxyl groups with molecular weights ranging from 1,000 to above 15,000. Poloxamers are sold under the tradename of Pluronic and Pluraflow by BASF including Poloxamer 407 and Pluraflow L4370.

Other emulsifying agents that may be used include polymeric emulsifiers such as the Pemulen® series available from B.F. Goodrich, and which are predominantly high molecular weight polyacrylic acid polymers useful as emulsifiers for hydrophobic substances.

Other optional agents that may be used include dimethicone copolys selected from alkyl- and alkoxy-dimethicone copolys, such as C12 to C20 alkyl dimethicone copolys and mixtures thereof, as aid in providing positive tooth feel benefits. An example is cetyl dimethicone copoly marketed under the trade name Abil EM90. The dimethicone copoly may be present from about 0.01% to about 25%, typically from about 0.1% to about 5% by weight.

The compositions may optionally contain a humectant, which functions for example to keep toothpaste compositions from hardening upon exposure to air. Certain humectants can also impart desirable sweetness and mouthfeel effects to compositions. Suitable humectants for use herein include glycerin, sorbitol, polyethylene glycol, propylene glycol, and other edible polyhydric alcohols. The humectant may comprise up to about 70%, typically from about 5% to 55%, by weight of the composition.

In some embodiments, the present compositions will comprise a high molecular weight (MW) polyethylene glycol, also called polyethylene oxide (PEO), which provides humectant and mouth moisturization benefits like the more commonly used species of PEO of relatively lower molecular weight (generally from about 200 to about 7000). The high molecular weight PEO’s with MW’s from about 200,000 to about 7,000,000 have been found to provide excellent mouth moisturization or anti dry mouth benefits as described in commonly assigned U.S. Application
61/257,677. The high MW PEO’s provide the anti dry mouth benefit by first lubricating the mouth. This lubrication or lubricity, meaning the lack of friction between elements in contact, provides the opposite effect of dryness. In addition, the high MW PEO’s provide actual mouth moisturization by retaining water. Other materials that have been used to treat dry mouth and/or to lubricate the mouth, such as carboxymethylcellulose, for example, do not retain water as well as high MW PEO’s. Furthermore, when high MW PEO’s are used in combination with polyol humectants (for example, glycerin, erythritol, xylitol, sorbitol, mannitol), a synergistic effect of better moisture retention is achieved, better than either PEO’s or polyols used alone, or better than simply an additive effect. It is believed the PEO’s are able to deliver superior moisture retention because the high MW PEO’s are retained particularly in the soft tissues of the mouth and not easily washed away. By contrast, usual polyol humectants are washed away quickly and perceived to moisturize for less than five minutes. PEO’s are retained in the mouth longer and consumer perception of the PEO’s moisturization benefit lasts significantly longer than with polyols. In combination with the present organophosphate, it is believed mixed deposition may occur, with the PEO intermingled with the organophosphate particularly on the tooth surface. Or a PEO layer may be deposited on top of the organophosphate layer or vice versa. The combination of PEO and organophosphate has been found to provide improved lubricity and moisturized feel as opposed to a dry mouth feel. The high molecular weight polyethylene oxide may be present for example, in an amount ranging from about 0.001% to about 5.0%, by weight.

Method of Use

The present invention also relates to methods of use to modify teeth and other oral surfaces to have increased hydrophobic character thereby imparting surface protection, improved tooth health, structure, appearance and textural benefits including erosion protection as well as one or more of caries prevention and control of bacterial activity in the oral cavity which cause undesirable conditions including plaque, calculus, gingivitis, periodontal disease and malodor. The benefits of these compositions may increase over time when the composition is used repeatedly. The method of use or treatment herein may comprise contacting a subject’s dental enamel surfaces and mucosa in the mouth with the oral compositions according to the present invention. The method may comprise brushing with a dentifrice or rinsing with a dentifrice slurry or mouthrinse. Other methods include contacting the topical oral gel, denture product, mouthspray, or other form with the subject’s teeth and oral mucosa. The subject may be any person or animal whose tooth surface is contacted with the oral composition. By animal is meant
to include household pets or other domestic animals, or animals kept in captivity. For example, a method of treatment may include a person brushing a dog’s teeth with a dentifrice composition.

**EXAMPLES**

The following examples further describe and demonstrate embodiments within the scope of the present invention. These examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention as many variations thereof are possible without departing from the spirit and scope.

Example I. Dentifrice Compositions

Dentifrice compositions I-A – I-G according to the present invention and a comparative example I-H (without organophosphate) are shown below with ingredients in weight %. These compositions are made using conventional methods.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>I-A</th>
<th>I-B</th>
<th>I-C</th>
<th>I-D</th>
<th>I-E</th>
<th>I-F</th>
<th>I-G</th>
<th>I-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerin</td>
<td>10.0</td>
<td>30.0</td>
<td>20.0</td>
<td>20.0</td>
<td>-</td>
<td>20.0</td>
<td>20.0</td>
<td>30.0</td>
</tr>
<tr>
<td>Sorbitol Solution</td>
<td>30.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>43.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Silica, dental type</td>
<td>15.0</td>
<td>15.0</td>
<td>15.00</td>
<td>15.0</td>
<td>22.0</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
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<tr>
<td>NaF (USP)</td>
<td>0.24</td>
<td>0.24</td>
<td>0.24</td>
<td>0.24</td>
<td>0.24</td>
<td>0.24</td>
<td>0.24</td>
<td>0.24</td>
</tr>
<tr>
<td>Potassium dodecyl phosphate (20% Soln)</td>
<td>10.0</td>
<td>10.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>10.0</td>
<td>10.0</td>
<td>-</td>
</tr>
<tr>
<td>Sodium dodeceth-1 phosphate (30% Soln)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.33</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sodium acid pyrophosphate</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sodium saccharin</td>
<td>0.5</td>
<td>0.50</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.50</td>
<td>0.5</td>
</tr>
<tr>
<td>Sucralose</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.12</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sodium hydroxide (50% soln)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Carboxymethyl cellulose</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Carbomer 956</td>
<td>0.3</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.2</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Polyethylene oxide</td>
<td>-</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>0.2</td>
<td>2.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Flavor</td>
<td>1.2</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Cetyl alcohol</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.0</td>
</tr>
<tr>
<td>Stearyl alcohol</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Na lauryl sulfate (28% soln)</td>
<td>-</td>
<td>-</td>
<td>4.0</td>
<td>-</td>
<td>4.0</td>
<td>-</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Cocoamidopropyl Betaine (30% soln)</td>
<td>-</td>
<td>-</td>
<td>4.0</td>
<td>3.33</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Petrolatum</td>
<td>-</td>
<td>30.0</td>
<td>40.0</td>
<td>40.0</td>
<td>-</td>
<td>5.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>USP Water, Color, Preservative</td>
<td>QS</td>
<td>QS</td>
<td>QS</td>
<td>QS</td>
<td>QS</td>
<td>QS</td>
<td>QS</td>
<td>QS</td>
</tr>
</tbody>
</table>

Example II. Multi-Phase Oral Care Products

Stable oral care products comprising two or more distinct compositions each contained in physically separate compartments of e.g., a dentifrice dispenser are shown below. Each product contains at least a first composition (II-A1 – II-A4) comprising one or more selected surface
active organophosphate compounds and at least a second composition (II-B1 – II-B6) comprising an incompatible active such as stannous, zinc and calcium cations. Formulating the negatively charged organophosphate with a cation together in a single composition could result in precipitation, which could render both the cation and organophosphate compound inactive and compromise their intended benefits. Formulating these incompatible ingredients in separate phases allows optimum delivery to the oral cavity of both cation and organophosphate agent.

<table>
<thead>
<tr>
<th>INGREDIENTS</th>
<th>II-A1</th>
<th>II-A2</th>
<th>II-A3</th>
<th>II-A4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Fluoride</td>
<td>0.24</td>
<td>0.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium Laureth -1- phosphate (30% Soln)</td>
<td>6.7</td>
<td>6.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium Lauryl phosphate (40% w/w)</td>
<td></td>
<td></td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Sorbitol (70% Soln)</td>
<td>60.0</td>
<td>60.00</td>
<td>60.0</td>
<td></td>
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<tr>
<td>Sodium phosphate tribasic</td>
<td>1.1</td>
<td>1.10</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>Sodium phosphate monobasic</td>
<td>0.42</td>
<td>0.42</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>Glycerin</td>
<td></td>
<td></td>
<td></td>
<td>30.0</td>
</tr>
<tr>
<td>Sodium Saccharin</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Sucralose</td>
<td></td>
<td></td>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>Zeodent 119</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td></td>
</tr>
<tr>
<td>Zeodent 109</td>
<td></td>
<td></td>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>Carbomer 956</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>2.0</td>
</tr>
<tr>
<td>CMC 7M8SF P&amp;G</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>Sodium lauryl sulfate (28% Soln)</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Hydrogen Peroxide (35% Soln)</td>
<td></td>
<td></td>
<td></td>
<td>8.57</td>
</tr>
<tr>
<td>Sodium Hydroxide (50%)</td>
<td></td>
<td></td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Flavor</td>
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<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>USP Water</td>
<td>QS</td>
<td>QS</td>
<td>QS</td>
<td>QS</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>INGREDIENTS</th>
<th>II-B1</th>
<th>II-B2</th>
<th>II-B3</th>
<th>II-B4</th>
<th>II-B5</th>
<th>II-B6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stannous Fluoride</td>
<td>0.91</td>
<td>0.91</td>
<td>0.91</td>
<td>0.91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sorbitol (70% Soln.)</td>
<td>42.0</td>
<td>40.0</td>
<td>40.0</td>
<td>32.0</td>
<td>64.47</td>
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</tr>
<tr>
<td>Gantrez S-95</td>
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<td>2.0</td>
<td>2.0</td>
<td>1.0</td>
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<tr>
<td>Zinc Lactate</td>
<td>0.67</td>
<td>0.67</td>
<td>2.5</td>
<td>2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium Chloride dihydrate</td>
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<td></td>
<td></td>
<td></td>
<td>0.73</td>
<td></td>
</tr>
<tr>
<td>Sodium hexametaphosphate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13.0</td>
</tr>
<tr>
<td>Sodium Gluconate</td>
<td>1.06</td>
<td>1.06</td>
<td>1.06</td>
<td>0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propylene Glycol</td>
<td></td>
<td></td>
<td></td>
<td>7.0</td>
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<td></td>
</tr>
<tr>
<td>Polyethylene Glycol 300</td>
<td></td>
<td></td>
<td></td>
<td>7.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glycerin</td>
<td></td>
<td></td>
<td></td>
<td>37.0</td>
<td>10.0</td>
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</tr>
<tr>
<td>Sodium Saccharin</td>
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<td>0.8</td>
<td>0.5</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Zeodent 119</td>
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<td>15.0</td>
<td>12.5</td>
<td>15.0</td>
<td>15.0</td>
</tr>
<tr>
<td>Zeodent 109</td>
<td></td>
<td></td>
<td></td>
<td>12.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xanthan Gum</td>
<td></td>
<td></td>
<td></td>
<td>0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydroxyethylcellulose</td>
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<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Carrageenan</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.6</td>
<td>0.7</td>
<td>0.7</td>
</tr>
</tbody>
</table>
Example III. Oral Care Compositions

Oral care compositions according to the present invention comprising an organophosphates and a comparative example (III-B) in the form of nonabrasive gels are shown below with ingredients in weight %. These compositions are made using conventional methods and may be used for example as finishing or sealing gels to prevent rapid washing away of actives that have been prior deposited on the surface.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>III-A</th>
<th>III-B</th>
<th>III-C</th>
<th>III-D</th>
<th>III-E</th>
<th>III-F</th>
<th>III-G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium dodecyl phosphate (30% Soln)</td>
<td>-</td>
<td>-</td>
<td>13.33</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Potassium dodecyl phosphate (20% Soln)</td>
<td>20.0</td>
<td>-</td>
<td>-</td>
<td>20.0</td>
<td>-</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Potassium laureth phosphate (40% Soln)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>22.0</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Glycerin</td>
<td>-</td>
<td>33.0</td>
<td>20.0</td>
<td>13.0</td>
<td>35.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Flavor</td>
<td>1.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Saccharin</td>
<td>2.0</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>2.0</td>
</tr>
<tr>
<td>Polyethylene oxide</td>
<td>-</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>-</td>
</tr>
<tr>
<td>Carbomer</td>
<td>-</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>Mineral Oil</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.0</td>
<td>-</td>
</tr>
<tr>
<td>Petrolatum</td>
<td>77.0</td>
<td>62.0</td>
<td>61.67</td>
<td>62.0</td>
<td>63.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Versagel</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>87.0</td>
</tr>
</tbody>
</table>

Example IV. Denture Care Products

Denture Care products in the form of denture adhesives (IV-A to IV-C) and denture cleansers (IV-D to IV-F) are shown below with ingredients in weight %. These compositions are made using conventional methods. The dental adhesive formulations may be prepared by heating the ingredients to about 65 °C, mixing together and filling the mixture into containers such as squeeze tubes. Various salts of AVE/MA polymer may be used, including Ca, Mg, Sr, Na, Zn, Fe salts or mixtures thereof. The denture cleanser formulations may be prepared by blending the ingredients together and forming the mixture into tablets using a tablet press or any other suitable tablet-making procedure well-known in the art. The levels of each ingredient in the examples may be varied by 5, 20, 25, 50, 100% or more. Furthermore, the example formulations of each type may be mixed with each other to provide hybrid-examples.
### Denture Adhesives

<table>
<thead>
<tr>
<th></th>
<th>IV-A</th>
<th>IV-B</th>
<th>IV-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkyl Vinyl Ether / Maleic Acid Polymer Salt [AVE/MA]</td>
<td>33.0</td>
<td>33.0</td>
<td>33.0</td>
</tr>
<tr>
<td>Mineral Oil</td>
<td>23.9</td>
<td>23.9</td>
<td>23.9</td>
</tr>
<tr>
<td>Petrolatum</td>
<td>19.7</td>
<td>16.9</td>
<td>11.9</td>
</tr>
<tr>
<td>Sodium Dodeceth-1 Phosphate (Dehydrated)</td>
<td>2.2</td>
<td>5.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Silicon Dioxide (Silica)</td>
<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Sodium CMC</td>
<td>Q.S.</td>
<td>Q.S.</td>
<td>Q.S.</td>
</tr>
</tbody>
</table>

### Denture Cleansers

<table>
<thead>
<tr>
<th></th>
<th>IV-D</th>
<th>IV-E</th>
<th>IV-F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetra Acetyl Ethylene Diamine [TAED]</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
</tr>
<tr>
<td>Sodium Perborate Monohydrate</td>
<td>17.5</td>
<td>17.5</td>
<td>17.5</td>
</tr>
<tr>
<td>Potassium Monopersulfate Granulated</td>
<td>48.2</td>
<td>48.2</td>
<td>48.2</td>
</tr>
<tr>
<td>Sodium Dodeceth-1 Phosphate (Dehydrated)</td>
<td>2.2</td>
<td>5.0</td>
<td>2.8</td>
</tr>
<tr>
<td>Tetra Sodium EDTA</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Sodium Lauryl Sulfoacetate</td>
<td>0.65</td>
<td>0.65</td>
<td>0.65</td>
</tr>
<tr>
<td>Hydrated Silica Amorphous</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Hydrogenated Rape Triglyceride</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Microcrystalline Cellulose</td>
<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Peppermint/ Other Mint Flavor</td>
<td>2.75</td>
<td>2.75</td>
<td>2.75</td>
</tr>
<tr>
<td>Granulated Pre-mix (1)</td>
<td>2.85</td>
<td>2.85</td>
<td>-</td>
</tr>
</tbody>
</table>

- Cetyl Dimethicone Copolyol 8.9
- Dimethicone Copolyol 11.0
- Peppermint 9.75
- Maize Starch Modified 52.0
- Silica Amorphous 1.0
- Sorbitol Q.S

<table>
<thead>
<tr>
<th></th>
<th>IV-D</th>
<th>IV-E</th>
<th>IV-F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granulated Pre-mix (2)</td>
<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
</tr>
</tbody>
</table>

- Sodium Carbonate 13.2
- Citric Acid 83.2
- Color 3.6

- Sodium Carbonate (Anhydrous) Q.S Q.S Q.S

The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as “40 mm” is intended to mean “about 40 mm”.

Every document cited herein, including any cross referenced or related patent or application, is hereby incorporated herein by reference in its entirety unless expressly excluded or otherwise limited. The citation of any document is not an admission that it is prior art with respect to any invention disclosed or claimed herein or that it alone, or in any combination with any other reference or references, teaches, suggests or discloses any such invention. Further, to the extent that any meaning or definition of a term in this document conflicts with any meaning
or definition of the same term in a document incorporated by reference, the meaning or definition assigned to that term in this document shall govern.

While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.
What is claimed is:

1. Use of a surface-active organophosphate compound in the manufacture of an oral care composition for modifying teeth and other oral surfaces to have increased hydrophobic character thereby imparting benefits of surface protection and improved tooth health, structure, appearance and texture, wherein the organophosphate compound is represented by the following general structure:

\[
Z^1 - O - P - O - Z^2
\]

\[
\downarrow
\]

\[
O - Z^3
\]

wherein \(Z^1\), \(Z^2\), or \(Z^3\) may be identical or different, \(Z^1\) represents an organic moiety selected from linear or branched alkyl, alkenyl, alkoxylated alkyl or alkoxylated alkenyl group of from 6 to 22 carbon atoms, preferably from 10 to 22 carbon atoms, optionally substituted by one or more phosphate groups; \(Z^2\) and \(Z^3\) each represents hydrogen, alkali metal, ammonium, protonated alkyl amine, protonated alkanolamine, or a \(Z^1\) group and wherein the surface-active organophosphate compound is present in an amount effective to provide an increase of at least 10 degrees in water contact angle of the surface and the hydrophobic character is maintained for a period of at least 5 minutes,

2. Use according to Claim 1, wherein the organophosphate compound is represented by the following structure wherein \(Z^1\) is an alkoxylated alkyl or alkoxylated group of formula

\[
R^1 - (OC_nH_{2n})_a(OC_mH_{2m})_b - (OC_nH_{2n})_a(OC_mH_{2m})_b
\]

\[
\downarrow
\]

\[
R^1 - (OC_nH_{2n})_a(OC_mH_{2m})_b - O - P - O - Z^2
\]

\[
\downarrow
\]

\[
O - Z^3
\]

wherein \(R^1\) represents a linear or branched alkyl or alkenyl group of from 6 to 22 carbon atoms, preferably from 10 to 22 carbon atoms, optionally substituted by one or more phosphate groups; \(n\) and \(m\), are individually and separately, 2 to 4; \(a\) and \(b\), individually and separately, are from 0 to 20 and \(a+b\) is at least 1, preferably \(a+b \leq 10\); \(Z^2\) and \(Z^3\) may be identical or different, each
represents hydrogen, alkali metal, ammonium, protonated alkyl amine or protonated alkanolamine, or a \( R^1-(OC_nH_{2n})_a(OC_mH_{2m})_b \) group.

3. Use according to any one of Claims 1 to 2 wherein the composition further comprises one or more hydrophobic materials selected from long chain hydrocarbon waxes and oils; synthetic ethylenic polymers; fatty alcohols; fatty ethers; fatty acids; fatty esters; silicone polymers; and fluoroorganopolymers.

4. Use according to any one of Claims 1 to 3 for providing one or more benefits selected from ease of cleaning; increased retention of oral care actives on teeth and other oral surfaces; improved resistance of teeth to bacterial or biofilm adhesion, erosive demineralization or dissolution, sensitivity and staining; prevention of tooth damage from subsequent exposure to erosive chemicals, abrasives and acids; improved smoothness, shine, glossiness, and clean feel of teeth; improved lubricity and mouth moisturization; and control of mucosal desquamation.

5. An oral care composition for modifying teeth and other oral surfaces to have increased hydrophobic character thereby imparting benefits of surface protection and improved tooth health, structure, appearance and texture, comprising
   
   (a) a surface-active organophosphate compound in an amount effective to provide an increase of at least 10 degrees in water contact angle of the surface and maintain the hydrophobic character for a period of at least 5 minutes, wherein the organophosphate compound is represented by the following general structure:

   \[
   Z^1-O-P-O-Z^2
   \]

   \[
   O-Z^3
   \]

   wherein \( Z^1, Z^2, \) or \( Z^3 \) may be identical or different, \( Z^1 \) represents an organic moiety selected from linear or branched alkyl, alkenyl, alkoxylated alkyl or alkoxylated alkenyl group of from 6 to 22 carbon atoms, optionally substituted by one or more phosphate groups; \( Z^2 \) and \( Z^3 \) each represents hydrogen, alkali metal, ammonium, protonated alkyl amine, protonated alkanolamine, or a \( Z^1 \) group,
   
   (b) one or more oral care agents, and
   
   (c) an orally acceptable carrier.
6. An oral care composition according to Claim 5, wherein the organophosphate compound is represented by the following structure, wherein \( Z^1 \) is an alkoxylated alkyl or alkoxyalkyl group of formula \( R^1-(OC_nH_{2n})_a(OC_mH_{2m})_b=- \):

\[
\begin{align*}
R^1-(OC_nH_{2n})_a(OC_mH_{2m})_b^- & \quad O-P-O-Z^2 \\
& \quad O-Z^3
\end{align*}
\]

wherein \( R^1 \) represents a linear or branched alkyl or alkenyl group of from 6 to 22 carbon atoms, preferably from 10 to 22 carbon atoms, optionally substituted by one or more phosphate groups; \( n \) and \( m \), are individually and separately, 2 to 4; \( a \) and \( b \), individually and separately, are from 0 to 20 and \( a+b \) is at least 1, preferably \( a+b \leq 10 \); \( Z^2 \) and \( Z^3 \) may be identical or different, each represents hydrogen, alkali metal, ammonium, protonated alkyl amine or protonated alkanolamine, or a \( R^1-(OC_nH_{2n})_a(OC_mH_{2m})_b^- \) group.

7. An oral care composition according to any one of Claims 5 or 6, further comprising one or more hydrophobic materials selected from long chain hydrocarbon waxes and oils; synthetic ethylenic polymers; fatty alcohols; fatty ethers; fatty acids; fatty esters; silicone polymers; and fluoroorganopolymers, preferably wherein the hydrophobic material comprises one or a mixture of petrolatum, mineral oil, microcrystalline wax, beeswax, lanolin, spermaceti, carnauba wax, polymethylene wax, polybutene, polyisobutene or a C12-C60 fatty alcohol.

8. An oral care composition according to any one of Claims 5 to 7 comprising two or more separate phases packaged in separate chambers of container, wherein a first phase comprises one or more oral care agents selected from cationic antimicrobial agents or a fluoride ion source and at least a second phase comprises the surface-active organophosphate compound.

9. An oral care composition according to any one of Claims 5 to 7 in the form of a dentifrice product comprising two or more thermodynamically stable but separate phases packaged together in a single container, wherein a first phase comprises a fluoride ion source in an aqueous carrier and a second phase comprises the surface-active organophosphate compound in a non-aqueous carrier, wherein the first phase is delivered to teeth before the second phase thereby delivering fluoride to teeth prior to exposure to the organophosphate.
10. An oral care composition any one of Claims 5 to 7, wherein the oral care agent comprises a polyethylene oxide having molecular weight ranging from 200,000 to 7,000,000 in an amount sufficient to provide mouth moisturization and anti dry mouth benefits.

11. An oral care composition according to any one of Claims 5 to 7 in the form of a non-abrasive sealing or finishing gel, wherein the organophosphate is present from 0.01% to 35% by weight.

12. An oral care composition according to any one of Claims 5 to 7 in the form of a denture cleanser or a denture adhesive, wherein the organophosphate is present from 0.01% to 35% by weight.