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(54) Toothpaste compositions

(57) Toothpaste compositions containing a soluble pyrophosphate salt as a anticalculus agent and potassium ions wherein such compositions are formulated to optimize the compatibility of potassium ions with the composition components comprise

(a) a safe and effective amount of a soluble pyrophosphate salt or mixture thereof;
(b) 5 - 60% of abrasive;
(c) Fluoride ion source to provide 50 - 3500 ppm fluoride ion;
(d) 5 - 60% of humectant chosen from sorbitol, glycerine, polyethylene glycols, mineral oil and mixtures thereof;
(e) 0.3 - 5% of surfactant comprising alkyl sulphate optionally ethoxylated;
and
(f) water, the composition being pH 6 - 10 and containing 0.5 - 7% potassium ions.

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ORAL COMPOSITIONS

TECHNICAL FIELD

The present invention relates to toothpaste compositions which provide an anticalculus benefit.

BACKGROUND OF THE INVENTION

Dental calculus, or tartar as it is sometimes called, is a deposit which forms on the surfaces of the teeth at the gingival margin. Supragingival calculus appears principally in the areas near the orifices of the salivary ducts; e.g., on the lingual surfaces of the lower anterior teeth and on the buccal surfaces of the upper first and second molars, and on the distal surfaces of the posterior molars.

Mature calculus consists of an inorganic portion which is largely calcium phosphate arranged in a hydroxyapatite crystal lattice structure similar to bone, enamel and dentine. An organic portion is also present and consists of desquamated epithelial cells, leukocytes, salivary sediment, food debris and various types of microorganisms.

As the mature calculus develops, it becomes visibly white or yellowish in color unless stained or discolored by some extraneous agent. In addition to being unsightly and undesirable from an aesthetic standpoint, the mature calculus deposits are regarded by many as a constant source of mechanical irritation of the gingiva.

A wide variety of chemical and biological agents have been suggested in the art to retard calculus formation or to remove calculus after it is formed. Mechanical removal of this material periodically by the dentist is, of course, routine dental office procedure.

The chemical approach to calculus inhibition generally involves chelation of calcium ion and/or crystal growth inhibition which prevents the calculus from forming and/or breaks down mature calculus by removing calcium.

U.S. Patent 4,515,712, May 7, 1985 to Parran et al. discloses oral compositions containing dialkali metal and mixtures of

dialkali metal and tetraalkali metal pyrophosphate salts. The prior art, however, is silent about the compatibility problems associated with the use of potassium ions in pyrophosphate salt systems. Potassium pyrophosphate, having a high degree of solubility in water, is an excellent pyrophosphate source. One big problem associated with potassium ions is the formation of an insoluble potassium alkyl sulfate. Other problems involve the incompatibility of potassium ions with alcohol and alcohol type components of a dentifrice.

It is an object of the present invention to provide compositions which deliver an effective anticalculus benefit.

It is a further object of the present invention to provide an effective anticalculus product utilizing compositions which are formulated to optimize the compatibility of potassium ions with the composition components. The formation of the aforementioned potassium alkyl sulfate precipitate is thereby minimized.

It is a further object of the present invention to provide an anticalculus product which does not inhibit remineralization of the teeth.

It is still a further object of the present invention to provide an effective method for treating calculus.

It is still a further object of the prevent invention to provide compositions which are cosmetically acceptable.

These and other objects will become more clear from the detailed description which follows.

All percentages and ratios used herein are by weight unless otherwise specified.

SUMMARY OF THE INVENTION

The present invention embraces an oral composition comprising:

a) a safe and effective amount of a soluble pyrophosphate salt;

b) from about 5% to about 60% of a suitable toothpaste abrasive;

c) an amount of a fluoride ion source sufficient to provide from about 50 ppm to about 3500 ppm fluoride;

d) from about 5% to about 60% of a humectant selected from the group consisting of sorbitol, glycerine, polyethylene glycols, mineral oil and mixtures thereof;

e) from about 0.3% to about 5% of a surfactant selected from the group consisting of alkyl sulfate surfactants, ethoxylated alkyl sulfate surfactants, and mixtures thereof; and

f) water,

wherein said composition has a pH of from about 6 to about 10, is substantially free of polyethylene glycols having 6 or fewer ethoxy groups and short chain monohydric alcohols and has potassium ions present at a level of 0.5% to about 7%.

DETAILED DESCRIPTION OF THE INVENTION

The compositions of the present invention comprise soluble pyrophosphate salts and potassium ions, which compositions are more stable than compositions which are not as carefully formulated.

By "safe and effective amount" as used herein, means sufficient compound to reduce calculus while being safe to the hard and soft tissues of the oral cavity.

By the term "comprising", as used herein, is meant that various additional components can be conjointly employed in the compositions of this invention as long as the pyrophosphate performs its intended functions.

Pyrophosphate Salts

The pyrophosphate salt used in the present compositions can be any of the alkali metal pyrophosphate salts. Specific salts include the alkali metal tetra alkali metal pyrophosphate, dialkali metal diacid pyrophosphate, trialkali metal monoacid pyrophosphate and mixtures thereof, wherein the alkali metals are preferably sodium or potassium. The salts are useful in both their hydrated and unhydrated forms. The amount of pyrophosphate salt useful in the present composition is any effective amount and is generally enough to provide at least 1.5% $P_2O_7^{-4}$ to the compositions. It is to be appreciated that the level of $P_2O_7^{-4}$ is

that provided to the composition and that other pyrophosphate forms (e.g., $HP_2O_7^{-3}$) may be present when the salt is totally dissolved and a pH established.

The pyrophosphate salts are described in more detail in Kirk & Othmer, Encyclopedia of Chemical Technology, Second Edition, Volume 15, Interscience Publishers (1968), incorporated herein by reference.

The potassium ions present in the compositions described herein may be provided by the pyrophosphate salts and a preferred salt is potassium pyrophosphate because of its excellent solubility. Mixtures of the tetra potassium salt with other pyrophosphate salts are also preferred.

Toothpaste Abrasive

The abrasives useful in the dentifrice compositions of the present invention include many different materials. The material selected must be one which has good compatibility with both fluoride ions and polyphosphate ions. In this respect the abrasive must be able to allow for the quantities of fluoride ions and polyphosphate ions indicated herein below. Suitable abrasives include beta-phase calcium pyrophosphate prepared in accordance with the teaching of Schweizer, U.S. Patent 3,112,247, November 26, 1963. The beta-phase calcium pyrophosphate is prepared by heating gamma-phase calcium pyrophosphate to 700-900°C to change at least 50% of the gamma-phase to beta-phase and then immediately cooling. Another class of abrasives for use herein is the particulate thermosetting polymerized resins as described in Cooley et al. in U.S. Patent 3,070,510, December 25, 1962. Suitable resins include, for example, melamines, phenolics, ureas, melamine-ureas, melamine-formaldehydes, urea-formaldehydes, melamine-urea-formaldehydes, cross-linked epoxides, and cross-linked polyester. Still other abrasives suitable for use in the dentifrice compositions include alumina and insoluble metaphosphates.

Silica dental abrasives, of various types, can provide the unique benefits of exceptional dental cleaning and polishing performance without unduly abrading tooth enamel or dentin.

Silica abrasive materials are also exceptionally compatible with sources of soluble fluoride. For these reasons they are preferred for use herein.

The silica abrasive polishing materials useful herein, as well as the other abrasives, generally have an average particle size ranging between about 0.1 to 30 microns, preferably 5 and 15 microns. The silica abrasive can be precipitated silica or silica gels such as the silica xerogels described in Pader et al., U.S. Patent 3,538,230, issued March 2, 1970 and DiGiulio, U.S. Patent 3,862,307, June 21, 1975, both incorporated herein by reference. Preferred are the silica xerogels marketed under the tradename "Syloid" by the W. R. Grace & Company, Davison Chemical Division. Preferred precipitated silica materials include those marketed by the J. M. Huber Corporation under the tradename, "Zeodent", particularly the silica carrying the designation "Zeodent 119". These silica abrasives are described in U.S. Patent 4,340,583, July 29, 1982, incorporated herein by reference.

The abrasive in the toothpaste compositions described herein is present at a level of from about 5% to about 60%, preferably from about 15% to about 25%.

Humectant

Sorbitol and glycerine are humectants useful in the present compositions. These materials generally are present at a level of from about 5% to about 20% on a individual basis and from about 5% to about 60% on a collective basis, based on a pure humectant basis. Additionally, polyethylene glycols may be used provided the number of ethoxy groups is greater than six. Mineral oil may also be used particularly mineral oils having a viscosity less than about 100 centipoise when measured at a temperature less than 100°F.

Surfactant

Toothpastes generally contain a surfactant to provide sudsing action to the paste when used. A common surfactant is an alkyl sulfate or an ethoxylated alkyl sulfate salt or a mixture thereof. The salts may include, for example, the sodium, potassium or ammonium salt. The alkyl sulfate (e.g. sodium C_{12}

alkyl sulfate) is very good at providing sudsing but presents problems when potassium ions are present due to the formation of an insoluble potassium alkyl sulfate. Even though the sodium salt of the surfactant may be used, when potassium ions are present, they will interchange with the sodium ions to form the potassium salt. The surfactant is generally present at a level of from about 0.3% to about 5%, preferably from about 0.5% to about 2% on a pure surfactant basis.

Fluoride Ion Source

Another essential component of the compositions herein is a fluoride ion source. The number of such sources is great and includes those disclosed in U.S. Patent 3,535,421, October 20, 1970 to Briner et al., incorporated herein by reference. Typical materials include: stannous fluoride, potassium fluoride, sodium fluoride, cesium fluoride, ammonium fluoride, aluminum fluoride, cupric fluoride, indium fluoride, stannous fluorozirconate, lead fluoride, ferrice fluoride, nickel fluoride, paladium fluoride, silver fluoride, zinc fluoride, zirconium fluoride, hexylamine hydrofluoride, laurylamine hydrofluoride, myristoxyamine, hydrofluoride, diethylaminoethyloctoylamide hydrofluoride, diethanolamineoethyloleylamide hydrofluoride, diethanolamino-propyl-N'-octadecenylamine dihydrofluoride, 1-ethanol-2-hexa-decylimidazoline dihydrofluoride, octoylethanolamine hydrofluoride, octyltrimethylammonium fluoride, dodecylethyldimethylammonium fluoride, tetraethylammonium fluoride, dilauryldimethylammonium fluoride. $\Delta^{8,9}$-octadecenylbenzyldimethylammonium fluoride, dioctyldiethylammonium fluoride, cyclohexylcetyldimethylammonium fluoride, furfuryllauryldimethylammonium fluoride, phenoxyethyl-cetyldimethylammonium fluoride, N:N'tetramethyl-N:N;-dilauryl-ethylenediammonium difluoride, N-cetylpyridinium fluoride, N"N-dilauryl-morpholinium fluoride, N-myristyl-N-ethyl-morpholinium fluoride, N-(octylaminocarbonylethyl)-N-benzyl-dimethylammonium fluoride, N(β-hydroxydodecyl) trimethyl-ammonium fluoride, N-phenyl-N-hexadecyldiethyl-ammonium fluoride, N-cyclohexyl-N-octadecyldimethylammonium fluoride, N-(2-carbocyclohexoxyethyl)-N-myristyldimethylammonium fluoride, N-(2-carbobenzyloxyethyl)-N-dodecyldimethylammonium fluoride,

N-[2-(N:N'-dimethylaminocarbonyl)-ethyl]-N-dodecyldiethylammonium fluoride, N-carboxymethyl-N-cicosyldimethylammonium fluoride, betaine hydrofluoride, sarcosine stannous fluoride, alanine stannous fluoride, glycine potassium fluoride, sarcosine potassium fluoride, glycine hydrofluoride, lysine hydrofluoride, sodium monofluoro phosphate and mixtures thereof. Sodium fluoride is the preferred fluoride source.

The amount of the fluoride ion source should be sufficient to provide from about 50 ppm to 3500 ppm, preferably from about 500 ppm to 3000 ppm of fluoride ions.

Water

Water is also present in the toothpastes of this invention. Water employed in the preparation of commercially suitable toothpastes should preferably be deionized and free of organic impurities. Water generally comprises from about 10% to 60%, preferably from about 20% to 40%, by weight of the toothpaste 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.

Potassium Ions

The potassium ions present in the compositions of this invention can be introduced into the compositions by means of the pyrophosphate salt(s) or other materials such as sweeteners, binders and flavors. The amount of potassium ions is related to the amount of alkyl sulfate or ethoxylated sulfate and is generally in the range of from about 0.5% to about 7%, preferably from about 1% to about 3%.

Optional Components

In preparing toothpastes, it is necessary to add some thickening material to provide a desirable consistency. Preferred thickening agents are carboxyvinyl polymers, carrageenan, hydroxyethyl cellulose and water soluble salts of cellulose ethers such as sodium carboxymethyl cellulose and sodium carboxymethyl hydroxyethyl cellulose. Natural gums such as gum karaya, 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 in an amount from 0.5% to 5.0% by weight of the total composition can be used.

Flavoring agents can also be added to toothpaste compositions. Suitable flavoring agents include oil of wintergreen, oil of peppermint, oil of spearmint, oil of sassafras, and oil of clove. Sweetening agents which can be used include aspartame, acesulfame, saccharin, dextrose, levulose and sodium cyclamate. Flavoring and sweetening agents are generally used in toothpastes at levels of from about 0.005% to about 2% by weight.

As was noted earlier, the compositions of the present invention are substantially free of polyethyleneglycols having fewer than about six ethoxy groups and short chain (e.g., methyl, ethyl, isopropyl) monohydric alcohols. By substantially free is meant less than about 2% of the materials are present.

Method of Manufacture

The compositions are made using conventional mixing techniques. A method is described in Example I.

COMPOSITION USE

The present invention in its method aspect involves applying to the oral cavity safe and effective amounts of the pyrophosphate salt. Generally an amount of at least about 1.9 grams of the material is effective.

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

EXAMPLE I

The following is a toothpaste representative of the present invention.

Component	Wt. %
Sorbitol (70% aqueous solution)	9.297
Double reverse osmosis water	28.129
Sodium fluoride	0.243
Sodium saccharin	0.300
Tetrapotassium pyrophosphate (65% aqueous solution)	4.967
Tetrasodium pyrophosphate	1.834
Sodium acid pyrophosphate	2.680
PEG-12	4.000
Titanium dioxide	0.500
Color	0.050
Flavor	1.000
Silica abrasive	21.000
Sodium alkyl sulfate (27% aqueous solution)	4.000
Gel slurry	22.000
Total	100.000

Gel Slurry	
Sorbitol (70% aqueous solution)	9.070
Glycerine	12.000
Iota carrageenan	0.770
Carbopol 940S[1]	0.160

[1]Carbopol 940S is a carboxyvinyl polymer offered by B. F. Goodrich Company.

The above composition is prepared by placing the main batch of sorbitol, water, sodium fluoride and sodium saccharin in a mix tank which is heated to from about 100°F to about 110°F. The heated mixture is mixed until clear. Sufficient time to reach clarity is about 10 to 15 minutes.

To the mixture is added the tetrapotassium pyrophosphate solution, the tetrasodium pyrophosphate and the sodium acid

pyrophosphate, in that order. This mixture is heated to from about 130°F to about 140°F and mixed for from about 5 to about 10 minutes until clarity is obtained.

The gel slurry is prepared at this time and is held for subsequent use.

After clarity is obtained in the main mix tank, the silica, surfactant, and gel slurry are added with the total mixture being heated to from about 160°F to about 170°F. Minor components (titanium dioxide, color and flavor) are then added and the final mixture mixed for about 15 minutes. The mixture is finally milled, deaerated and packed into dispersion.

EXAMPLE II

The following is a toothpaste representative of the present invention.

Component	Wt. %
Sorbitol (70% aqueous solution)	2.510
Double reverse osmosis water	34.916
Sodium fluoride	0.243
Sodium saccharin	0.300
Tetrapotassium pyrophosphate (65% aqueous solution)	4.967
Tetrasodium pyrophosphate	1.834
Sodium acid pyrophosphate	2.680
PEG-12	4.000
Titanium dioxide	0.500
Color	0.050
Flavor	1.000
Silica abrasive	21.000
Sodium alkyl sulfate (27% aqueous solution)	4.000
Gel slurry	22.000
Total	100.000

Gel Slurry	
Sorbitol (70% aqueous solution)	6.070
Glycerine	15.000
Iota carrageenan	0.770
Carbopol 940S	0.160

EXAMPLE III

The following is a toothpaste representative of the present invention.

Component	Wt. %
Mineral oil	3.753
Double reverse osmosis water	33.641
Sodium fluoride	0.243
Sodium saccharin	0.288
Tetrapotassium pyrophosphate (65% aqueous solution)	4.967
Tetrasodium pyrophosphate	1.834
Sodium acid pyrophosphate	2.680
PEG-12	4.000
Titanium dioxide	0.500
Color	0.050
Flavor	1.044
Silica abrasive	21.000
Sodium alkyl sulfate (27% aqueous solution)	4.000
Gel slurry	22.000
Total	100.000

Gel Slurry	
Mineral oil	9.070
Glycerine	12.000
Iota carrageenan	0.770
Carbopol 940S	0.160

EXAMPLE IV

The following is a toothpaste representative of the present invention.

Component	Wt. %
Sorbitol (70% aqueous solution)	14.500
Double reverse osmosis water	26.959
Sodium fluoride	0.243
Sodium saccharin	0.320
Tetrapotassium pyrophosphate (65% aqueous solution)	8.470

Sodium acid pyrophosphate	2.680
Titanium dioxide	0.500
Color	0.050
Flavor	1.000
Silica abrasive	22.000
Sodium ethoxylated aklyl sulfate (30% aqueous solution)	5.000
Gel slurry	18.278
Total	100.000

Gel Slurry

Sorbitol	7.200
Glycerine	10.278
Iota carrageenan	0.650
Carbopol 940S	0.150

WHAT IS CLAIMED IS:

1. An oral composition in the form of a toothpaste effective in reducing calculus comprising:
   a) a safe and effective amount of a soluble pyrophosphate salt or mixture of said salts;
   b) from about 5% to about 60% of a suitable toothpaste abrasive;
   c) an amount of a fluoride ion source sufficient to provide from about 50 ppm to about 3500 ppm fluoride;
   d) from about 5% to about 60% of humectant selected from the group consisting of sorbitol, glycerine, polyethylene glycols, mineral oil, and mixtures thereof;
   e) from about 0.3% to about 5% of a surfactant selected from the group consisting of alkyl sulfate surfactants, ethoxylated alkyl sulfate surfactants and mixtures thereof; and
   f) water,

wherein said composition has a pH of from about 6 to about 10, is substantially free of polyethylene glycols having fewer than six ethoxy units and short chain monohydric alcohols and has potassium ions present at a level of from about 0.5% to about 7%.

2. An oral composition according to Claim 1 wherein the soluble pyrophosphate salt is selected from the group consisting of tetrapotassium pyrophosphate, tetrasodium pyrophosphate, sodium acid pyrophosphate and mixtures thereof.

3. An oral composition according to Claim 2 wherein the abrasive is selected from the group consisting of beta phase calcium pyrophosphate, silica, thermosetting resins, alumina and insoluble metaphosphates.

4. An oral composition according to Claim 3 wherein the fluoride ion source is sodium fluoride.

5. An oral composition according to Claim 4 wherein the humectant is a mixture of sorbitol and glycerine.

6. An oral composition according to Claim 5 wherein the surfactant is selected from the group consisting of sodium alkyl sulfate, ammonium alkyl sulfate and mixtures thereof.

7. An oral composition according to Claim 5 wherein the surfactant is selected from the group consisting of sodium ethoxylated alkyl sulfate, ammonium ethoxylated alkyl sulfate and mixtures thereof.

8. An oral composition according to Claim 6 wherein the pyrophosphate salt is tetrapotassium pyrophosphate.

9. An oral composition according to Claim 8 wherein the abrasive is a silica abrasive.

10. An oral composition according to Claim 1 wherein the soluble pyrophosphate salt is capable of providing at least about 1.5% $P_2O_7^{-4}$ to said composition.

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