

Oral Compositions

Technical Field

The present invention relates to oral compositions. In particular, it relates to so-called baking soda dentifrice compositions containing pyrophosphate anticalculus agents and which have improved stability and aesthetics.

Background

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 dentin. 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 colour unless stained or discoloured by some extraneous agent. This is undesirable from an aesthetic standpoint.

Mechanical removal of calculus periodically by the dentist is routine dental office procedure. A variety of chemical and biological agents have also been suggested to retard calculus formation or to remove calculus after it is formed. Pyrophosphate salts are chemical agents known to have the ability to retard calculus formation as described, for example, in U.S. Patent 4,999,184, to Parran, Jr. et al., issued March 12, 1991, the disclosure of which is incorporated herein by reference in its entirety.

Dentifrice compositions containing pyrophosphate salts and sodium bicarbonate (aka, baking soda) are also known, having been described for

example, in U.S. Patent 5,180,576, to Winston et al., issued January 19, 1993, the disclosure of which is incorporated herein by reference in its entirety. Obtaining stable dentifrice compositions containing sodium bicarbonate and pyrophosphate effective for inhibiting dental calculus formation, however, presents a processing challenge. Pyrophosphate dissolved in these dentifrice compositions is subsequently likely to recrystallize in the form of tetrasodium pyrophosphate decahydrate crystals. These crystals can grow into large, glass-like particles which have negative aesthetics and also have tartar control efficacy concerns.

U.S. Patent 5,180,576 (incorporated hereinbefore) apparently recognises this problem and describes avoiding it by a manufacturing process whereby the sodium bicarbonate is used to salt out the alkali metal pyrophosphate. The amount of dissolved pyrophosphate salt is therefore said to be relatively low in the final composition and the remaining pyrophosphate particles are said to be undissolved tetrasodium pyrophosphate decahydrate salted out by the sodium bicarbonate. These undissolved pyrophosphate crystals dissolve very quickly, however, when the composition is diluted with water as occurs during use. This then is just another way of practicing the invention disclosed and claimed, for example, in U.S. Patent 4,684,518, to Parran, Jr. et al., issued August 4, 1987, the disclosure of which is incorporated herein by reference in its entirety.

It is also known from PCT application US94/03280 that pyrophosphate/sodium bicarbonate-containing dentifrice compositions which are aesthetically acceptable and efficacious may be prepared by controlling the process conditions to insure that less than about 20% of the pyrophosphate is solubilized at any point in the process mixture. In practice, the process described in the above application still leads to solubilization of about 5% of the total pyrophosphate level. In order to minimise the risk of recrystallization of pyrophosphate decahydrate crystals, it would be desirable to reduce the soluble pyrophosphate level still further.

It is therefore an object of the present invention to provide an easily controlled process for preparing a stable dentifrice composition

containing sodium bicarbonate and pyrophosphate salts. An object is also to provide stable dentifrice compositions containing sodium bicarbonate and tetrasodium pyrophosphate salt particles of predetermined and/or consistent size. Another object of this invention is to prepare such stable compositions by a process controlling the processing conditions such that the level of pyrophosphate ion dissolved in the composition is less than 100 ppm, preferably less than 10 ppm.

These and other objects of the present invention will become readily apparent from the detailed description which follows.

All percentages and ratios used herein are by weight, and all measurements are made at 25°C, unless otherwise specified.

Summary of the Invention.

According to a first aspect of the invention, there is provided a dentifrice composition comprising:

- a) from about 5% to about 50% by weight of sodium bicarbonate;
 - b) a soluble fluoride ion source in an amount sufficient to provide from about 10ppm to about 3500ppm of fluoride ion;
 - c) at least about 1.5% by weight of tetrasodium pyrophosphate, of which some or all of the tetrasodium pyrophosphate is in the form of undissolved anhydrous tetrasodium pyrophosphate particles; and
 - d) from about 50% to about 94% dentifrice carrier materials;
- and wherein further said composition has a soluble pyrophosphate ion content in the range from about 1 to about 100ppm, preferably from about 1.5 to about 10ppm, more preferably from about 2 to about 5ppm.

The present invention also relates to a method of making the above dentifrice composition comprising the steps of:

- a) forming a premix of dentifrice carrier materials comprising one or more materials selected from binder/thickening agents, humectants, buffering agents, abrasive polishing materials, surfactants, sweetening agents, flavoring agents, titanium dioxide,

and mixtures thereof, said premix including at least one or more binder/thickening agents and one or more buffering agents sufficient to provide a pH in step b) hereof greater than about pH 8;

- b) forming a paste by adding water to the premix in an amount sufficient to hydrate the binder/thickening agent;
- c) adding sodium bicarbonate to the resulting paste;
- d) thereafter adding tetrasodium pyrophosphate, all at once or in portions, to the paste at a temperature less than about 30°C, preferably less than about 25°C and preferably at a pH of greater than about pH8.

Preferably, the tetrasodium pyrophosphate is added to the mixture after all other sodium-containing salts present in the composition have been added thereto. In preferred embodiments, moreover, the binder/thickening agent and buffering agent are added batchwise to the premix so as to provide multiple alternate layers of binder/thickening agent and buffering agent in the final premix, this being valuable from the viewpoint of achieving optimum paste rheology during the binder hydration step.

The present invention relates to a method of manufacturing a baking soda dentifrice composition containing pyrophosphate tartar control agent. The dentifrice compositions produced by the present process may be in the form of toothpastes or gels. The term "toothpaste", as used herein, means paste and gel formulations unless otherwise specified. The present invention also relates to baking/pyrophosphate tartar control dentifrice compositions comprising anhydrous tetrasodium pyrophosphate particles.

The present process and compositions comprise several essential components, as well as optional components. A detailed description of these components and the present process conditions are described hereinafter.

A) Pyrophosphate Salts

The pyrophosphate salts used in the present process and compositions must include tetrasodium pyrophosphate. This material

may be the anhydrous salt form or the decahydrate form, or any other species stable in solid form in the dentifrice compositions. The salt is 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.

While tetrasodium pyrophosphate salt particles are a necessary component of the present process and compositions, it is to be recognised that low levels of other pyrophosphate salts may be included in the process and compositions. Specific salts include tetra alkali metal pyrophosphate other than tetrasodium pyrophosphate, dialkali metal diacid pyrophosphates, trialkali metal monoacid pyrophosphate and mixtures thereof, wherein the alkali metals are sodium or potassium. (Pyrophosphate salts are described in more detail in Kirk & Othmer, Encyclopedia of Chemical Technology, Second Edition, Volume 15, Interscience Publishers (1958), incorporated herein by reference in its entirety). These salts are useful in both their hydrated and unhydrated forms. Because such salts are typically more soluble than the tetrasodium pyrophosphate salt, their inclusion in the process and compositions of the invention should be limited to avoid preparing compositions containing soluble pyrophosphate ion, and exclusion of such more soluble salts is preferred.

The amount of pyrophosphate salt useful in these compositions is any tartar control effective amount, and is generally enough to provide at least about 1.0%, preferably from about 1.5% to about 10%, more preferably from about 3.0% to about 6% $P_2O_7^{4-}$, by weight of the compositions. It is to be appreciated that the level of $P_2O_7^{4-}$ is that amount capable of being provided to the composition (i.e., the theoretical amount at an appropriate pH) and that other pyrophosphate forms (e.g., $HP_2O_7^{3-}$) may be present when a final product pH is established. The level of tetrasodium pyrophosphate salt preferably used in the present methods and compositions is therefore from about 1.5% to about 15%, and more preferably from about 2% to about 10%, by weight of the dentifrice composition.

B) Sodium Bicarbonate

Sodium bicarbonate, also known as baking soda, is a household product with a variety of uses including use in dentifrices and mouthrinses. It is a white powder that is soluble in water and unless stabilised, tends to release carbon dioxide in an aqueous system. The present compositions contain from about 5% to about 50%, preferably from about 10% to about 30% sodium bicarbonate by weight of composition.

C) Soluble Fluoride Ion Source

A soluble fluoride ion source is also incorporated in the present compositions. The soluble fluoride ion source is used in amounts sufficient to provide from about 10 to about 3500 ppm of the fluoride ion. Preferred fluorides are sodium fluoride, stannous fluoride, indium fluoride, and sodium monofluorophosphate. Norris et al., U.S. Patent 2,946,1735, issued July 26, 1960 and Widder et al., U.S. Patent 3,678,154, issued July 18, 1972 disclose such salts as well as others. Both patents are incorporated herein by reference in their entirety.

D) Dentifrice Carrier Materials

In preparing the present toothpaste process compositions, it is desirable to add one or more dentifrice carrier materials to the compositions. The term "dentifrice carrier materials", as used herein, means any material safe and effective for use in the toothpaste compositions prepared according the present invention. Such materials are well known in the art and are readily chosen by one skilled in the art based on the physical and aesthetic properties desired for the dentifrice composition being prepared. Dentifrice carrier materials typically comprise from about 50% to about 94%, preferably from about 60% to about 80% by weight of the present compositions.

The present compositions typically contain a binder/thickening material to provide a desirable consistency. Preferred binder/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, xanthan gum, gum arabic, and gum tragacanth can also be used. Colloidal magnesium aluminium silicate or finely

divided silica can be used as part of the thickening agent to further improve texture. Thickening agents can be used in an amount from about 0.2% to about 5.0% by weight of the total composition.

It is also desirable to include some humectant material in a toothpaste to keep the composition from hardening upon exposure to air. Certain humectants can also impart a desirable sweetness or flavour to toothpaste compositions. Suitable humectants include glycerin, sorbitol, other edible polyhydric alcohols, and mixtures thereof, at a level of from about 15% to about 70% by weight of composition.

Titanium dioxide can also be added to the present compositions. Titanium dioxide is a white powder which adds pigment to the compositions. Titanium dioxide generally comprises from about 0.25% to about 1% by weight of composition.

Water is also present in the compositions of this process. Water employed in the preparation of commercially suitable toothpastes should preferably be deionized and free of organic impurities. Water generally comprises from about 12% to about 45%, preferably from about 15% to about 35%, more preferably from about 20% to about 30% by weight of composition. These amounts of water include the free water which is added plus that which is introduced with other materials such as with sorbitol.

The pH of the present compositions is adjusted through the use of buffering agents. Buffering agents, as used herein, refer to agents that can be used to increase the pH of the compositions to a range of above about pH 8 as preferred for addition of the sodium bicarbonate and tetrasodium pyrophosphate. These agents include trisodium phosphate, sodium hydroxide and sodium carbonate. Sodium carbonate is preferred at a level of from about 0.5% to about 2% by weight of composition.

An abrasive polishing material can also be included. The abrasive polishing material contemplated for use in the compositions of the present invention can be any material which does not excessively abrade dentin. These include, for example, silicas including gels and precipitates,

calcium carbonate, dicalcium orthophosphate dihydrate, calcium pyrophosphate, tricalcium phosphate, calcium polymetaphosphate, insoluble sodium polymetaphosphate, hydrated alumina, and resinous abrasive materials such as particulate condensation products of urea and formaldehyde, and others such as disclosed by Cooley et al. in U.S. Patent 3,070,510, December 25, 1962, incorporated herein by reference. Mixtures of abrasives can also be used.

Silica dental abrasives, of various types are preferred because of their unique benefits of exceptional dental cleaning and polishing performance without unduly abrading tooth enamel or dentin. The silica abrasive polishing materials, useful herein, as well as the other abrasives, generally have an average particle size ranging between about 0.1 and 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 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 is preferably present at a level of from about 6% to 70%, more preferably from about 15% to about 25% by weight.

The toothpaste compositions can also contain surfactants. Suitable surfactants are those which are reasonably stable and foam throughout a wide pH range, including non-soap anionic, nonionic, cationic, zwitterionic and amphoteric organic synthetic detergents. Many of these suitable agents are disclosed by Gieske et al. in U.S. Patent 4,051,234, September 27, 1977, incorporated herein by reference. Sodium alkyl sulphate and polyethylene glycol are preferred for use herein at a level of about 4% to about 3% by weight of compositions respectively.

Flavouring agents can also be added to the present compositions. Suitable flavouring 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. Flavouring and sweetening agents are generally used in toothpastes at levels of from about 0.005% to about 2% by weight of composition.

The present invention compositions can also contain optional pharmaceutical agents (e.g., triclosan) and other tartar control agents. Optional tartar control agents include such known materials as 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., the disclosures of which are incorporated herein by reference in their entirety; as well as, e.g., polyamino propane sulfonic acid (AMPS)), polyphosphates (e.g. tripolyphosphate; hexametaphosphate), diphosphonates (e.g. EHDP; AHP), polypeptides (such as polyaspartic and polyglutamic acids), and mixtures thereof.

The toothpaste compositions are prepared by mixing together the components described above according to the method of manufacturing. This method comprises the steps of:

- a) forming a premix of dentifrice carrier materials comprising one or more materials selected from binder/thickening agents, humectants, buffering agents, abrasive polishing materials, surfactants, sweetening agents, flavoring agents, titanium dioxide, and mixtures thereof, said premix including at least one or more binder/thickening agents and one or more buffering agents sufficient to provide a pH in step b) hereof greater than about pH 8;
- b) forming a paste by adding water to the premix in an amount sufficient to hydrate the binder/thickening agent;
- c) adding sodium bicarbonate to the resulting paste;
- d) thereafter adding tetrasodium pyrophosphate, all at once or in portions, to the paste at a temperature less than about 30°C, preferably less than about 25°C and at a pH of greater than about pH8.

Preferably, the amount of pyrophosphate dissolved in the mixture for the methods and composition of the present invention is in the range from about 1 to about 100ppm, preferably from about 1.5 to about 10ppm, more preferably from about 2 to about 5ppm, measured as pyrophosphate ion. A method of measuring the amount of pyrophosphate dissolved in the mixture and compositions is described and exemplified hereinafter in the Examples.

The following examples further describe and demonstrate embodiments within the scope of the present invention.

EXAMPLES

The following are examples of paste and gel dentifrices having a pyrophosphate ion content of about 3.3%.

<u>Ingredient</u>	<u>Paste</u>	<u>Gel</u>
Sodium Bicarbonate	20.000	20.000
Water	19.773	19.773
Silica	15.000	15.000
Glycerin	15.000	15.000
Sorbitol (70%)	14.061	14.111
Tetrasodium Pyrophosphate	5.045	5.045
Sodium Alkyl Sulphate (28%)	4.000	4.000
PEG-6	3.000	3.000
Sodium Carbonate	1.250	1.250
Flavour	1.000	1.000
CarboxymethylCellulose	0.800	0.800
Sodium Saccharin	0.400	0.400
Titanium Dioxide	0.350	0.000
Sodium Fluoride	0.321	0.321
FD & C Blue No. 1	0.000	0.300

The paste compositions are prepared as follows. To the humectants (sorbitol, glycerine, PEG-6) at ambient temperature is added a particulate mix of sodium saccharin, sodium fluoride, sodium

carbonate, sodium carboxymethylcellulose and titanium dioxide, the sodium carbonate and sodium carboxymethylcellulose (CMC) being each added to the particulate mix in two equal batches in the order carbonate, CMC, carbonate, CMC to provide a so-called "layered" particulate mixture. To this liquid premix is then added water in amount sufficient to hydrate the binder, followed by silica. To this mixture is added sodium bicarbonate, followed by tetrasodium pyrophosphate, in solid form. The final paste product is then obtained by addition of flavour and sodium alkyl sulphate solution.

Measurement of the level of soluble pyrophosphate in these compositions is accomplished as follows.

3.00g $\pm$ 0.001g toothpaste is weighed into a 50ml polypropylene centrifuge tube; deionised water (9.0ml) and six glass beads are then added. Stopper and thoroughly mix for exactly 2 minutes on the vortex mixer. Transfer the contents to a 25ml centrifuge tube, stopper and spin at 15,000rpm at 10°C for 15 minutes. Pipette 1.0ml of the clear supernatant into a 100ml volumetric flask and dilute to volume with deionized water, mixed well. Dilute 10ml of this solution with deionized water and mix well. Analyse by ion chromatography.

CLAIMS

1. A dentifrice composition comprising:
 - a) from about 5% to about 50% by weight of sodium bicarbonate;
 - b) a soluble fluoride ion source in an amount sufficient to provide from about 10ppm to about 3500ppm of fluoride ion;
 - c) at least about 1.5% by weight of tetrasodium pyrophosphate, of which some or all of the tetrasodium pyrophosphate is in the form of undissolved anhydrous tetrasodium pyrophosphate particles; and
 - d) from about 50% to about 94% dentifrice carrier materials; and wherein further said composition has a soluble pyrophosphate ion content in the range from about 1 to about 100ppm.
2. A dentifrice composition according to Claim 1 wherein the dentifrice carrier materials comprise one or more materials selected from binder/thickening agents, humectants, water, buffering agents, abrasive polishing materials, surfactants, sweetening agents, flavoring agents, titanium dioxide, and mixtures thereof.
3. A dentifrice composition according to Claim 2 wherein the buffering agent is selected from trisodium phosphate, sodium hydroxide, sodium carbonate, and mixtures thereof.
4. A dentifrice composition according to any of Claims 1 to 3 wherein comprising from about 1.5% to about 15% tetrasodium pyrophosphate.
5. A dentifrice composition according to any of Claims 1 to 4 wherein said composition has a soluble pyrophosphate ion content in the range from about 1.5 to 10ppm.
6. A method of making a dentifrice composition according to any of Claims 1 to 5 comprising the steps of:
 - a) forming a premix of dentifrice carrier materials comprising one or more materials selected from binder/thickening agents,



humectants, buffering agents, abrasive polishing materials, surfactants, sweetening agents, flavoring agents, titanium dioxide, and mixtures thereof, said premix including at least one or more binder/thickening agents and one or more buffering agents sufficient to provide a pH in step b) hereof greater than about pH 8;

- b) forming a paste by adding water to the premix in an amount sufficient to hydrate the binder/thickening agent;
 - c) adding sodium bicarbonate to the resulting paste;
 - d) thereafter adding tetrasodium pyrophosphate, all at once or in portions, to the paste at a temperature less than about 30°C, preferably less than about 25°C and at a pH of greater than about pH8.
7. A method according to Claim 6 wherein the tetrasodium pyrophosphate is added to the mixture after all other sodium-containing salts present in the composition have been added thereto.
8. A method according to Claim 6 or 7 wherein the buffering agent comprises sodium carbonate.
9. A method according to any of Claims 6 to 8 wherein the binder/thickening agent and buffering agent are added batchwise to the premix so as to provide multiple alternate layers of binder/thickening agent and buffering agent in the final premix.



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(21) International Application Number: PCT/US96/00526 (22) International Filing Date: 5 January 1996 (05.01.96) (30) Priority Data: 9500746.4 ✓ 14 January 1995 (14.01.95) GB (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): LAYER, Teresa, May [GB/GB]; 7 Fountain Gardens Osborne Road, Windsor, Berkshire SL4 3SZ (GB). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AZ, BY, KZ, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: ORAL COMPOSITIONS (57) Abstract A dentifrice composition comprising: a) from about 5 % to about 50 % by weight of sodium bicarbonate; b) a soluble fluoride ion source in an amount sufficient to provide from about 10ppm to about 3500ppm of fluoride ion; c) at least about 1.5 % by weight of tetrasodium pyrophosphate, of which some or all of the tetrasodium pyrophosphate is in the form of undissolved anhydrous tetrasodium pyrophosphate particles; and d) from about 50 % to about 94 % dentifrice carrier materials; and wherein further said composition has a soluble pyrophosphate ion content in the range from about 1 to about 100ppm.		