# ZINC CONTAINING DENTIFRICE OF REDUCED ASTRINGENCY

## BACKGROUND OF THE INVENTION

1. Field of the Invention



*159159*

The present invention relates to a dentifrice composition useful for reducing oral malodor and more particularly a low astringent breath freshening oral care product for the treatment of oral malodor containing a combination of zinc and pyrophosphate salts.

Oral malodor, or halitosis, is caused by the putrefactive activity of microorganisms on appropriate substrate components of dental plaque, debris adhering to mucous membranes and salivary cellular elements to produce volatile sulfur compounds primarily hydrogen sulfide, methyl mercaptan and traces of methyl sulfide.

The incorporation of zinc salts into oral dental care products to beneficially reduce oral malodor is well known in the art, as for example, US Pat. Nos. 4,138,477 and 5,000,944. However, the astringency of zinc salts is a major drawback in its use in oral dental care products creating an unpleasant astringent taste in the mouth.

US 4,138,477 discloses a zinc salt containing oral composition of reduced astringency wherein the composition contains a zinc-polymer complex formed by the reaction of a zinc salt with an anionic polymer containing carboxylic, sulfonic and/or phosphonic acid radicals.

US 5,000,944 discloses a zinc containing antitartar oral product substantially free of astringency, containing as the essential agent, a zinc/polyphosphate complex having at least about a 50% water solubility, formed by reaction of a zinc salt with a potassium or sodium polyphosphate salt by dissolving a zinc salt in a polyphosphate solution such as pyrophosphate, tripolyphosphate, hexametaphosphate and combinations thereof.



*G00002*

A drawback to zinc/polyphosphate complex salts is that although astringency is substantially reduced, dentifrices containing zinc and polyphosphate salts have a propensity towards instability, wherein during storage, polycrystalline lumps form, such formation being believed to be caused by the aggregation of crystals of the zinc-polyphosphate complex. These lumps are visible to the naked eye, have a substantial hardness so that the spontaneous formation of these zinc/polyphosphate crystals are highly undesirable and detrimental to consumer acceptance of the dental product. Therefore, there is a need in the art for a means whereby both the stability and astringency characteristics of oral care products containing zinc salts can be improved so that such products will be more acceptable for use by consumers.

## SUMMARY OF THE INVENTION

In accordance with the present invention there is provided a stable aqueous oral care composition for the treatment of oral malodor having limited astringency, the composition comprising an orally acceptable vehicle containing a complex formed from zinc salt, anionic polycarboxylate polymer and a pyrophosphate salt ingredients incorporated in to the oral care composition.

As will hereinafter be demonstrated, the presence of the zinc anionic polycarboxylate polymer pyrophosphate complex in the oral care product unexpectedly provides a stable product of substantially reduced astringency having improved palatability when used by the consumer.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the practice of the present invention, the source of zinc ion used to form the zinc/anionic polycarboxylate polymer/pyrophosphate complex in the oral care composition is generally a zinc salt that is fully or partially soluble in water, including zinc nitrate, zinc sulfate, zinc citrate, zinc chloride, zinc citrate being preferred. The zinc salt is generally incorporated in the oral care composition of the present invention at a concentration of about 1 to about 5% by weight and preferably about 1.5 to about 3% by weight.

Anionic polycarboxylate polymers used to form the zinc/anionic polycarboxylate polymer/pyrophosphate complex are generally employed in the form of their free acids or preferably partially or fully neutralized water soluble alkali metal (e.g., potassium and preferably sodium) or ammonium salts. Preferred are 1:4 to 4:1 copolymers of maleic anhydride or acid with another polmerizable ethylenically unsaturated monomer, preferably methylvinylether/maleic anhydride having a molecular weight (M.W.) of about 30,000 to about 1,800,000 most preferably about 30,000 to about 700,000. Examples of these copolymers are available from ISP Corporation under the tradename Gantrez, e.g., AN 139 (M.W. 500,000), AN 119 (M.W. 250,000); S-97 Pharmaceutical Grade (M.W. 700,000), AN 169 (M.W. 1,200,000-1800,000), and AN 179 (M.W. above 1,800,000); wherein the preferred copolymer is S-97 Pharmaceutical Grade (M.W. 700,000).

The anionic polycarboxylate polymer is employed in amounts effective to form the zinc-polymer-pyrophosphate complex within the oral composition. To this end, the anionic polycarboxylate polymer is incorporated in the oral care composition from about 0.1% to about 10% by weight, preferably from about 0.2% to about 3.0% by weight.

Pyrophosphate salts used to prepare the zinc/anionic polymer/pyrophosphate complexes include dialkali or tetraalkali metal pyrophosphate salts such as $Na_2P_2O_7$, $KaP_2O_7$, $Na_2K_2P_2O_7$, $Na_2H_2P_2O_7$ and $K_2H_2P_2O_7$. The pyrophosphate salts are included in the oral composition of the present invention at a concentration of about 1 to about 5% by weight and preferably about 0.5 to about 3% by weight.

To prepare a dentifrice composition of the present invention, the zinc salt anionic polycarboxylate polymer and pyrophosphate salt ingredients are incorporated in the oral care product which includes a vehicle which contains water, humectant, surfactant and a polishing agent.

The humectant is generally a mixture of humectants, such as glycerol, sorbitol and polyethylene glycol of molecular weight in the range of 200-1000, but other mixtures of humectants and single humectants may also be employed. The humectant content is in the range about of 10% to about 80% by weight and preferably about 30 to about 50% by weight. The water content is in the range of about 10 to about 25% by weight.

Inorganic thickeners may be included in the dentifrice component in which potassium salts are included as an ingredient include fumed silicas such as Cabosil

available from Cabot Corporation, and thickening silicas including those available from Crosfield Chemicals designated Sorbosil TC-15 or Sylox 15 from W.R. Grace.

Organic thickeners of natural and synthetic gums may be incorporated in the oral care composition of the present invention. Examples of such thickeners are carrageenan (Irish moss), xanthan gum, sodium carboxymethyl cellulose, starch, polyvinylpyrrolidone, hydroxyethylpropylcellulose,hydroxybutyl methyl cellulose, hydroxypropyl methyl cellulose, and hydroxyethyl cellulose. The organic thickener may be incorporated in the compositions of the present invention at a concentration of about 0.25 to about 2% by weight and preferably about 0.5 to about 1% by weight.

Surfactants may be incorporated in the oral care product of the present invention included as an ingredient to provide foaming properties. The surfactant is preferably anionic, suitable examples of which include higher alkyl sulfates such as potassium or sodium lauryl sulfate which is preferred, higher fatty acid monoglyceride monosulfates, such as the salt of the monosulfated monoglyceride of hydrogenated coconut oil fatty acids, alkyl aryl sulfonates such as sodium dodecyl benzene sulfonate, higher fatty sulfoacetates, higher fatty acid esters of 1,2 dihydroxy propane sulfonate, and the substantially saturated higher aliphatic acyl amides of lower aliphatic amino carboxylic acid compounds, such as those having 12 to 16 carbons in the fatty acid, alkyl or acyl radicals, and the like. Examples of the last mentioned amides are N-lauroyl sarcosine, and the salts of N-lauroyl, N-myristoyl, or N-palmitoyl sarcosine. The surfactant is generally present in the oral care compositions of the present invention at a concentration of about 0.5 to about 5.0% by weight.

Abrasives may be incorporated in the oral composition of the present invention and preferred abrasives are siliceous materials, such as silica. A preferred silica is a precipitated amorphous hydrated silica, such as Sorbosil AC-35, marketed by Crosfield Chemicals, or Zeodent 115 and Zeodent 165 from Huber Company but other abrasives may also be employed, including sodium metaphosphate, potassium metaphosphate, tricalcium phosphate, calcium phosphate dihydrate, anhydrous dicalcium phosphate, calcium pyrophosphate, magnesium orthophosphate, calcium carbonate, sodium bicarbonate, alumina trihydrate, aluminum silicate, calcined alumina and bentonite. The concentration of abrasive in the oral composition of the present invention will normally be in the range of 5 to about 40% by weight and preferably 10 to 30% by weight.

Other ingredients which may be incorporated in the oral care composition of the

present invention, include pigment, sweetener, flavor and preservative. In white dental cream formulations, the pigment of choice is titanium dioxide, rutile, and the proportion thereof will normally be in the range of 0.5 to 1.25% by weight, preferably 0.75 to 1 % by weight. The sweetener content will normally be that of an artificial or synthetic sweetener and the normal proportion thereof present will be in the range of 0.1 to 1% by weight, preferably 0.3 to 0.5% by weight. The flavor content, which is preferably of a mixed peppermint/menthol flavor, will usually be in the range of 0.5 to 2% by weight, preferably 0.5 to 1.5% by weight. F.D. & C Grade dyes may be used in appropriate amounts to provide desired colors. The contents of other components or adjuvants of the potassium salt containing dentifrice will normally not exceed 10% by weight, often will be less than 5% by weight, and can be as low as 0%.

To prepare the oral composition of the present invention, the zinc salt is added to a mixture of water, humectants and anionic polycarboxylate polymer and dispersed in a conventional mixer until the mixture becomes a slurry which is smooth in appearance. The pyrophosphate salt may also be added at this point, preferably predissolved as a water solution. Other water soluble ingredients such as fluoride salts and sweeteners such as sodium saccharin may also be added at this point. This mixture may be heated to 100-110°F and mixed for 10 to 30 minutes producing a homogeneous gel phase. The mixture is transferred to a vacuum mixer. The abrasive is then added and mixed for 10 to 30 minutes at high speed under a vacuum in the range of 5 to 100 millimeter of mercury pressure, preferably 5 to 50 mm Hg, providing a homogenous mixture. The surfactant and flavor are then added to the paste which is followed by mixing another 10 to 20 minutes under vacuum of 5 to 50 mm Hg. The resultant product is a stable astringent dentifrice of a texture like that of normal toothpastes or gels having a pH in the range of 5 to 8, preferably 6.5 to 7.5, e.g., 7, and of satisfactory flavor.

The following Example is further illustrative of the present invention, but it is understood that the invention is not limited thereto. All amounts referred to herein and the appended claims are by weight.

**Example**

An aqueous dentifrice was prepared by admixing the ingredients listed in the Table below.

**TABLE**

| Ingredient | Wt.% |
|---|---|
| Deionized Water | 17.54 |
| Zinc citrate trihydrate | 2.00 |
| Gantrez S-97 (13% soln.) | 11.54 |
| PEG 600 | 3.00 |
| Glycerin | 11.50 |
| Carrageenan | 0.400 |
| Sodium carboxymethyl cellulose | 0.60 |
| Sorbitol (70% soln.) | 24.60 |
| Sodium Saccharin | 0.300 |
| Tetrasodium pyrophosphate | 2.0 |
| Titanium Dioxide | 1.00 |
| Sodium fluoride | 0.32 |
| Silica | 22.20 |
| NaOH (50% soln.) | 0.60 |
| Flavor | 1.20 |
| Sodium Lauryl Sulfate | 1.20 |
| **Totals** | 100.00 |

After storage of the dentifrice in sealed plastic tubes for 8 weeks at 40°F, room temperature, 105°F and 120°F, no formation of crystalline material was noted.

The astringency and palatability of the dentifrice was evaluated by a flavorist for attributes such as astringency and taste acceptability as compared to a commercial non-astringent antibacterial dentifrice which did not contain zinc ion and a commercial dentifrice known to be astringent containing 2% by weight zinc citrate.

The flavorist rated the dentifrice as having minor astringency.

By way of contrast, when the dentifrice of the Example was prepared in which the zinc citrate was incorporated in the dentifrice composition together with 1% by weight tetrasodium pyrophosphate and 7% by weight of sodium tripolyphosphate and the anionic polycarboxylate polymer Gantrez S-97 was not included in the dentifrice composition, the composition had low astringency but undesirable crystals formed in the dentifrice within 15 days when stored in plastic tubes at room temperature.

## CLAIMS

What is claimed is:

1. A stable, zinc containing aqueous oral composition having low astringency, the composition comprising an orally acceptable vehicle containing a complex formed in the vehicle from a zinc salt, an anionic polycarboxylate polymer and a pyrophosphate salt whereby less astringency is experienced by the user of the composition.

2. The composition of claim 1 wherein the zinc salt is zinc citrate.

3. The composition of claim 1 wherein the pyrophosphate salt is tetrasodium pyrophosphate or tetrapotassium pyrophosphate.

4. The composition of claim 1 wherein the anionic polycarboxylate polymer is a vinyl ether/maleic anhydride copolymer.

5. The composition of claim 1 wherein the copolymer is present in the composition at a concentration of about 0.1 to about 10% by weight.

6. The composition of claim 4 wherein the zinc salt is present in the composition at a concentration of about 1 to about 5% by weight.

7. The composition of claim 1 wherein the pyrophosphate salt is present in the composition at a concentration of about 0.5 to about 3.0% by weight.

8. A method for preparing stable, zinc containing oral composition having low astringency, which comprises preparing an orally acceptable vehicle containing water and humectants and admixing a zinc salt, an anionic polycarboxylate polymer and a pyrophosphate salt with the vehicle to form a zinc/anionic polycarboxylate/pyrophosphate complex whereby less astringency is experienced by the user of the composition.

9. The method of claim 8 wherein the zinc salt is zinc citrate.

10. The method of claim 8 wherein the pyrophosphate salt is tetrasodium pyrophosphate or tetrapotassium pyrophosphate.

11. the method of claim 8 wherein the anionic polycarboxylate polymer is a vinyl ether/maleic anhydride copolymer.

12. The method of claim 11 wherein the copolymer is present in the composition at a concentration of about 0.1 to about 10% by weight.

13. The method of claim 8 wherein the zinc salt is present in the composition at a concentration of about 1 to about 5% by weight.

14. The method of claim 8 wherein the pyrophosphate salt is present in the composition at a concentration of about 0.5 to about 3.0% by weight.