Abstract

Fluoride-containing toothpaste which does not liberate oxygen in the presence of water, which is free or essentially free of mineral oil and animal and vegetable triglyceride oils, and having improved tooth cleaning properties comprising an abrasive agent, in major proportion based upon the weight of the solid ingredients of the toothpaste, a small percentage of a fluorine-containing compound, and at least 20%, by weight, of the total of the liquid ingredients of said toothpaste, of at least one water-soluble polyoxyalkylene glycol having an average molecular weight of at least 200.

21 Claims, No Drawings
FLUORIDE-CONTAINING TOOTHPASTE

This application is a continuation-in-part of application Ser. No. 31,789, filed April 24, 1970, now Pat. No. 3,703,578 dated Nov. 21, 1972.

This invention relates to improved toothpastes of the type which contain fluoride-containing compounds and which, therefore, possess the well known advantages as to caries inhibiting properties arising from said fluoride-containing compounds. The toothpastes of the present invention are, additionally, in their particularly advantageous embodiments, characterized by substantially enhanced cleaning properties with low abrasion characteristics. The toothpastes are based upon special formulations which also make for a stable system for said fluoride-containing compounds so that they can maintain their effectiveness over prolonged storage times and a variety of storage conditions.

Conventional toothpaste formulations comprise a mixture of a number of solid ingredients with a mixture of a number of liquid ingredients all of which, together, produce a product of suitable paste consistency. The solid ingredients of the toothpaste formulation comprise one or more abrasives, and, in certain cases, detergents and miscellaneous ingredients such as gums, sweeteners, thickeners, etc., the abrasive constituting at least the major proportion, that is, in excess of 50%, by weight, of the total of the solid ingredients of the toothpaste formulation. The liquid ingredients of the toothpaste formulation usually comprise water, humectant, and, commonly, very minor constituents such as flavors or flavoring oils.

Numerous efforts have been made to provide toothpastes which clean the teeth rapidly as well as impart an enhanced polish. One of such approaches lies in the selection of the abrasive ingredient or ingredients of the toothpaste formulation. The use of relatively harsher abrasives will sometimes result in a more rapid and more complete cleaning of the teeth brushed with toothpastes containing the same that if abrasives with a milder abrading action are used in the toothpastes. This type of approach to bring about more rapid and more complete cleaning of the teeth is, generally, not preferred because of the adverse effects on exposed dentin and oral health.

Accepted Dental Therapeutics 1969/70, published by the American Dental Society, discusses the function of an abrasive and states the "Dentifrices should certainly be free from very harsh abrasives, such as materials that can scratch enamel." It further states "there has been a recent tendency to promote dentifrices on the basis of their ability to whiten or brighten teeth. Such claims appear to relate almost exclusively to the incorporation in the dentifrices of harsher abrasive agents such as calcium carbonate, anhydrous dibasic calcium phosphate, or silica. Highly abrasive products should not be used regularly by individuals having exposed cementum or dentin, or possibly, by individuals with restored tooth surfaces of the softer synthetic materials." It concludes that "there would appear to be no valid reason for use of a dentifrice with a greater abrasiveness than is necessary to prevent residual accumulation on the teeth."

An early report concerning the abrasion properties of dentifrice cleaning and polishing agents was made in a paper entitled "Experiments and Observations on the Wasting of Tooth Tissue Variously Designated as Erosion Abrasion, Chemical Abrasion, Denudation, Etc., 10 15 20 25 30 35 40 45 50 55 60 65

"Dent. Cosmos, 49:1–23; 109–124; 225–247; 1907, the author concluding commonly used dentifrices at that time were capable of producing damage to the teeth. Similar results were obtained by various later investigators.

Studies have also been made on the necessity of an abrasive in a dentifrice. Manly, R. S.: A Structureless Recurrent Deposit on Teeth, J. Dent. Res. 22:479–486, 1943, and McCauley et al., Clinical Efficacy of Powder and Paste Dentifrices, J. Amer. Dent. Assoc. 33:993–997, 1946, noted a high incidence of pellicle in persons using a nonabrasive dentifrice. Phillips and Van Huyzen: Dentifrices and the Tooth Surface, Amer. Perf. 50:33–41, 1948, reported a high incidence of tooth discoloration from the collection of material on the tooth surface. Vallotton, C. F.: An Acquired Pigmented Pellicle of the Enamel Surface, J. Dent. Res. 24:161–169, 1945, and Kitchin, P. C., and Robinson, H. B. G.: How Abrasive Need a Dentifrice Be? J. Dent. Res. 27:501–506, 1948, reported that the teeth of about two thirds of the persons using a liquid dentifrice with no abrasive system had a variety of stains. Kitchin and Robinson in the same paper also found that only 4% of subjects brushing with water alone failed to form stains within a two week period. Dudding et al: Patient Reactions to Brushing Teeth with Water, Dentifrice, or Salt and Soda, J. Periodont 31:386–392, 1960, found that toothbrushing without the use of a dentifrice resulted in pellicle formation in 93% of the subjects after a five week study compared to only 9% when a dentifrice was used. Kitchin and Robinson, in their evaluation of the ability of commercial dentifrices to prevent pellicle formation, suggested that the cleaning ability was related to abrasiveness to dentin.

It is apparent from the foregoing studies on abrasion and cleaning that the usual method of increasing tooth cleaning generally results in a dentifrice having a high level of abrasion for dentin.

The abrasiveness of a dentifrice has most recently been determined by the so-called RDA method of Gravenstetter, et al., in their paper The Measurement of the Abrasion of Human Teeth by Dentifrice Abrasion: A Test Utilizing Radioactive Teeth, J. Dent. Res. 37:1060–1068, 1958. This method utilizes freshly extracted human teeth, which are irradiated, producing the radio nuclide, P14, a high energy Beta emitter with a half life of 14.3 days. This irradiated tooth is brushed with a mechanical toothbrush, across the den.
been made to embody in toothpastes ingredients which inhibit or reduce dental caries. Possibly the most widely used caries reducing or inhibiting ingredients in toothpastes are those which provide a fluoride ion as, for instance, stannous fluoride. A significant problem which has been encountered in incorporating fluoride ions, through the use of fluoride-containing inorganic compounds, into toothpastes has been the fact that the abrasive or polishing ingredient or ingredients of the toothpaste reacts with the fluoride-containing inorganic compounds, usually slowly or gradually and over a period of time, which may be weeks or months, to inactivate said fluoride-containing compounds, apparently by forming insoluble compounds which do not ionize to release fluoride ions. Such insoluble compounds have no caries reducing or inhibiting properties in that they do not bring about desired enamel hardening effects on the tooth enamel. Hence, such toothpastes have poor storage properties in that they lose their intended caries reducing or inhibiting effects over a period of time.

Certain procedures have heretofore been evolved, as shown in various prior art patents and publications, to meet the aforesaid problem associated with incorporating fluoride-containing compounds into toothpastes. Thus, in U.S. Pat. No. 2,876,166, it is shown that such abrasive or polishing agents as calcium orthophosphate, if heat treated to convert it into calcium pyrophosphate or certain other molecularly dehydrated calcium phosphates, will, when used as the abrasive or polishing agent in toothpastes containing fluoride-containing compounds, make for much greater availability of fluoride ions than if the conventional nonheat treated calcium orthophosphate was used. Other approaches designed to meet this problem are disclosed in U.S. Pat. Nos. 3,227,617 and 3,308,029.

Sodium fluoride is perhaps one of the most difficult fluoride-containing dental caries inhibiting agents to effectively incorporate into a toothpaste in which the abrasive or polishing agent is a calcium compound, whereas stannous fluoride does not, generally speaking, present as great difficulties. This appears to be due to the fact that sodium fluoride is entirely ionic, whereas, in stannous fluoride, the fluoride bond has a substantial covalent character. Nevertheless, certain special toothpaste compositions have been suggested utilizing sodium fluoride in conjunction with certain metaphosphates wherein the sodium fluoride is reasonably stable and is capable of inhibiting dental caries by reducing enamel solubility.

It has been discovered, in accordance with the present invention, that certain combinations of ingredients comprising abrasive agents, fluoride-containing compounds, and a water-soluble polyoxyalkylene glycol, without any mineral oil or vegetable or animal triglycerides, oils, in a toothpaste exhibit improved properties with respect to the matter of stability of the fluoride-containing compounds over prolonged periods of time. The compositional environment of the toothpastes of the present invention is of a character such that a wide variety of fluoride-containing compounds maintain their stability to a substantial extent in the presence of a wide variety of abrasive or polishing agents. In addition, where mild abrasives are utilized, the toothpastes of the present invention also surprisingly exhibit enhanced cleaning and luster-impacting properties in relation to tooth surfaces. While toothpaste formulations can be made in accordance with our invention which contain substantially no water, our invention also contemplates toothpaste formulations which contain proportions of water, generally up to about 10%, while still maintaining excellent stability of the fluoride-containing compound or compounds.

The toothpaste compositions of the present invention contain a very substantial, generally a major, proportion of one or more abrasives based on the weight of the solids of the toothpaste formulation, and, generally, at least 20%, by weight of the total of the liquid ingredients of the toothpaste formulation, of one or more polyoxyalkylene glycols described in detail below. While, in certain cases, polyoxyalkylene glycols may constitute the liquid ingredients, and the total liquid ingredients, of the toothpaste, they may constitute only a part of the liquid ingredients of the toothpaste formulation, not less than 20% by weight of said liquid ingredients and, better still, from 35% to 60% of the total weight of the liquid ingredients of the toothpaste. In other cases, the polyoxyalkylene glycols utilized are semi-solid or solid at room temperature. Based on the weight of the finished toothpaste, the polyoxyalkylene glycols will usually most desirably comprise from about 20% to about 30% although the percentages may be somewhat lower, usually not below about 15%, or somewhat higher, usually not more than about 45%.

Various of them can be represented by the formula

\[ \text{HO—Alk—O—(Alk—O)}_n\text{H} \]

where Alk is an alkylene radical containing from 2 to 4 carbon atoms, namely, ethylene, propylene or butylene, especially ethylene, and n is an integer such that the average molecular weight of the polyoxyalkylene glycol is at least 200 and so that the polyoxyalkylene glycol is reasonably water-soluble or is soluble in the liquid ingredients of the toothpaste formulation, hereafter, for convenience, encompassed by the term “water-soluble.” In the case of the polyoxyethylene glycols, the subscript n is at least 4 and can be materially greater than 4 and, indeed, up to the point where the polyoxyethylene glycol is a solid at room temperature. Illustrative polyoxyalkylene glycols which are useful in the production of toothpastes in accordance with our invention are polyoxyethylene glycols having average molecular weights of about 200, 350, 400, 500, 600, 700, 800, 900 and 1,000 and, as stated above, still higher in certain cases. Mixtures of the aforesaid polyoxyalkylene glycols can also be utilized. Furthermore, polyoxyalkylene glycols can be used in which there are present ethoxy and propoxy groups, or ethoxy and butoxy groups, or propoxy and butoxy groups, or all three of such groups as, for instance, 1 mole of tetraethyleneglycol added with 1 mole of propylene oxide and 1 mole of polyoxyethylene glycol 400 added with 1 mole of propylene oxide. Particularly satisfactory are polyoxyethylene glycols having average molecular weights between about 600 and about 800, or 650 to 750, those having an average molecular weight of about 700 being especially satisfactory. It may be noted that the viscosity, in centipoises and measured at 70°F, of a polyoxyethylene glycol which has an average molecular weight of about 600, (Polyethyleneglycol 600), is about 11,000, and it is a semi-solid at 70°F or room temperature; and that a polyoxyethylene glycol having an average molecular weight of 700 or higher is a solid at 70°F or room temperature.
It is, at times, desirable to include with said latter polyoxyethylene glycols, in any given toothpaste formulation made in accordance with the present invention, a smaller proportion of higher polyoxyethylene glycols, such as those of an average molecular weight of about 2,000 to about 6,000, generally in the range of about 5 to 12% by weight of the toothpaste. The polyoxyalkylene glycols utilized pursuant to the present invention are not surfactants or surface active agents in the sense of which such terms are commonly used in the art. For purposes of the present invention, the polyoxyalkylene glycols employed in the practice of the present invention will, in a 1% solution in water at 25°C, not reduce the surface tension of water to below 45 dyne/cm.

The dry ingredients of the toothpastes of the present invention contain one or more abrasives such as precipitated calcium carbonate, dicalcium phosphate dihydrate, dicalcium phosphate anhydrous, dibasic calcium phosphate, tribasic calcium phosphate, calcium pyrophosphate, calcium sulfate, hydrated alumina, silica, insoluble sodium metaphosphate, and the like, the abrasive constituting the major proportion of the total of the dry ingredients or the major proportion of the total of the solids of the toothpaste formulation. The RDA values of the abrasives selected are desirably not above about 400, and should not be in excess of 200 best results in accordance with the present invention. Particularly satisfactory is dicalcium phosphate dihydrate with an RDA value of about 125 to 150. The RDA value of the finished toothpaste, in its particularly advantageous embodiments, is not in excess of 200 and, better still, is in the range of about 90 to about 150.

The fluoride-containing or fluoride compounds which can be used in accordance with the present invention are, per se, known to the art for use in reducing or inhibiting dental caries. They comprise, generally speaking, fluoride-containing compounds which normally dissociate to yield fluoride ions in aqueous solution, and they include, among others, such inorganic compounds as alkali metal fluorides such as sodium fluo-
ride, potassium fluoride and lithium fluoride, stannous fluoride, stannous chlorofluorides, sodium mono-
fluorophosphate and stannous fluorozirconate. They are shown in such U.S. Pat. Nos. 2,839,448; 2,876,166; 2,946,725; 3,227,617; 3,227,618; 3,226,867; 3,266,996 and 3,308,029, the disclosures with respect to said fluorides being incorporated herein by reference. Especially satisfactory are stannous fluo-
ride, titanium tetrafluoride and tin (II) octafluorozirconate. The proportions thereof are, in all cases, small and will usually be employed in amounts to provide at least 0.1%, by weight, of ionizable fluoride and gener-
ally not more than 0.4%, by weight, total fluoride. In the case of stannous fluoride, for instance, the amount thereof will be in the range of about 50 to 3,000 parts per million based on the weight of the toothpaste with a good average being about 1,000 to about 1,500 parts per million. The percentages are not critical and are in-
dicated in the foregoing patents. The fluoride-
containing compounds are a part of the dry ingredients of the toothpaste formulation.

In addition, commonly it is the practice to include one or more detergents or surfactants in the toothpaste formulation and where such is a normally solid prod-
uct, or contains solids, as will usually be the case, it is considered as constituting a dry ingredient of the toothpaste formulation. Commonly used detergents or surfactants include, by way of illustration, soaps, sodium lauryl sulfate, sodium lauryl sulfate, sulfococul-
rate, sodium range of sulfated monoglyceride (of coco-
nut oil fatty acids), and sodium N-lauroyl sarcosinate.

Other normally solid ingredients which, commonly, are incorporated into toothpastes are binders, which are usually hydrophilic colloids. Among such binders are, for instance, gum arabic, ghatti, gum karaya, gum tragacanth, Irish moss, (Na) alginites, bentonite, Vee-
gum, methyl cellulose and sodium carboxymethyl-
cellulose. In a limited aspect of the present invention, it has been found that metallic, particularly aluminum, soaps of fat-forming fatty acids, especially aluminum stearate, are exceptionally satisfactory, aluminum soaps, such as aluminum octoate or aluminum stearate appearing to coat with the polyoxyalkylene glycols to further enhance the polish and lustre of the brushed teeth, and also functioning effectively to stabilize the paste character of the toothpaste at the elevated tempera-
tures which are at times encountered in shipping and storage of the toothpastes. Where employed, they will usually be used in a proportion of about 1 to about 12% by weight of the toothpaste. Where aluminum soaps are included in the toothpaste formulations of the present invention, care must be exercised, if water is to be incorporated into the toothpaste formulation, that too much water be not employed since it may destroy the desired gel structure imparted by the aluminum soaps. In any event, the binder selected must be one which will swell in the toothpaste mixture of ingredi-
ents into which it is incorporated.

The liquid ingredients of the toothpastes of the present invention, in addition to such water-soluble polyox-
ylkylene glycols as may be normally liquid at room temperature, desirably also include one or more of glycerin, propylene glycol and sorbitol solutions, or mixtures of the same, which are utilized for, in addition to their well-known humectant properties, their ability to improve taste and mouth feel. In certain cases, it may be desirable to include small proportions of water which, generally, will not be in excess of about 5% but, in certain cases, may be appreciably greater, of the weight of the liquid ingredients of the formulation, in the toothpaste formulations of our invention. The water serves mainly to counteract or reduce possible adverse tastes that may otherwise tend to be imparted to the toothpaste by particular polyoxyalkylene glycols which are utilized in said toothpastes.

Various supplemental ingredients can, of course, be incorporated into the toothpastes to obtain particular effects and they may be of liquid or solid character. Il-
lustriative of such supplemental ingredients are perfumes, dyes or other colorants, chloroform or flavoring chloroform, and enzymes, etc.

The following examples are illustrative of toothpastes in accordance with the present invention. It will be under-
stood that numerous other toothpastes can be made following the guiding principles and teachings disclosed herein. Unless otherwise specified, all parts are in terms of weight.

Individual Examples are made by combining, in each case, the aforesaid composition with 46.52 parts of the identified fluoride-containing compound, poly-
3,885,028

Example A

<table>
<thead>
<tr>
<th>Parts</th>
<th>Polyoxyethylene glycol 4000</th>
<th>Dicalcium Phosphate Dihydrate</th>
<th>Aluminium Stearate</th>
<th>Sodium Saccharin</th>
<th>Methyl &quot;PARABEN&quot; (methyl ester of para-hydroxy benzoic acid)</th>
<th>Propyl &quot;PARABEN&quot; (propyl ester of para-hydroxy benzoic acid)</th>
<th>&quot;MAPROFIX&quot; 563</th>
<th>(anhydrous sodium lauryl sulphate)</th>
<th>Flavoring</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>40</td>
<td>5</td>
<td>0.75</td>
<td>0.18</td>
<td>0.05</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>53.48</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The balance (46.52%) is comprised of:

<table>
<thead>
<tr>
<th>Fluoride Salt</th>
<th>PEG700</th>
<th>96% Glycerin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂PO₃F</td>
<td>0.76</td>
<td>22.88</td>
</tr>
<tr>
<td>SnF₂</td>
<td>0.40</td>
<td>23.06</td>
</tr>
<tr>
<td>NaF</td>
<td>0.20</td>
<td>23.16</td>
</tr>
<tr>
<td>CaPO₃F</td>
<td>0.943</td>
<td>22.789</td>
</tr>
<tr>
<td>K₃PO₃F</td>
<td>0.962</td>
<td>22.779</td>
</tr>
<tr>
<td>TiF₄</td>
<td>0.163</td>
<td>23.179</td>
</tr>
<tr>
<td>KPO₄F</td>
<td>0.40</td>
<td>23.06</td>
</tr>
<tr>
<td>ZrF₂SnF₅</td>
<td>0.332</td>
<td>23.094</td>
</tr>
</tbody>
</table>

Any suitable procedure can be used to produce the toothpaste from the above formulation. One suitable way is to place the polyoxyethylene glycol 4000, the polyoxypropylene glycol 700 and the glycerin in a mixer and heat to about 55° to 60°C to provide a liquid mixture. The mixture is transferred to another container and allowed to cool to about 35°C under conditions of mixing. The dicalcium phosphate dihydrate, the sodium saccharin, the fluoride-containing compound, the methyl PARABEN and the propyl PARABEN are then blended in, with stirring, then the aluminium stearate is added, a vacuum of about 25 inches is drawn and mixing is effected at high speed for about 20 minutes after which the MAPROFIX 563 is added. The mixing is continued under stirring for about 3 to 5 minutes. The temperature rises to about 50°C during the two last-mentioned mixing steps. The flavoring is mixed in, and then the mixture is pumped into a large tank from which it is filled into conventional toothpaste containers.

Other well known mixing procedures for producing toothpastes can be employed, as such or with minor variations. Thus, for instance, the binder, previously wetted with the humectants, is admixed, under slight heating if desired, with and dispersed in the remaining liquid portion of the toothpaste formulation (except for the flavoring) containing the sodium saccharin and such preservative as may be utilized. The resulting gel is then admixed, in a suitable mixer, with a premixture of the abrasive and the fluoride-containing compound, said premixture being added gradually to the gel, until homogeneity is obtained. Finally, the flavor and the detergent are added and mixed uniformly through the mass. The latter may then be milled, deaerated, and filled into toothpaste tubes.

Example B

<table>
<thead>
<tr>
<th>Parts</th>
<th>Polyoxypropylene glycol 700</th>
<th>Dicalcium Phosphate Dihydrate</th>
<th>Glycerin</th>
<th>Lauryl Sodium Sulfate</th>
<th>Carboxyvinyl polymer</th>
<th>Stannous Fluoride</th>
<th>Sodium Saccharin</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.25</td>
<td>41.5</td>
<td>23.25</td>
<td>2</td>
<td>1</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Example C

<table>
<thead>
<tr>
<th>Parts</th>
<th>Polyoxyethylene glycol 600</th>
<th>Aluminium Hydroxide Gel (20% water)</th>
<th>Titanium Tetrafluoride</th>
<th>Lauryl Sodium Sulfate</th>
<th>Sodium Saccharin</th>
</tr>
</thead>
<tbody>
<tr>
<td>22.3</td>
<td>52.85</td>
<td>23</td>
<td>0.15</td>
<td>1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Toothpaste compositions made in accordance with the present invention exhibit excellent stability of the fluoride-containing compositions. Thus, in the following Table I tests are shown of toothpastes made as described in Example A, using various fluoride-containing compounds in varying proportions and over varying periods of storage at different illustrative temperatures. The ionic fluoride levels in the cases of SnF₂, NaF, TiF₄ and ZrF₂SnF₅ were excellently maintained with relatively minor losses over a period of 26 weeks. In the cases of KPO₄F, Na₂PO₃F and K₃PO₃F, the ionic fluoride levels dropped off appreciably, particularly at the higher temperatures but, even here, a reasonable level was maintained. In this connection, it may be pointed out that conventional dentifrices containing, for instance, sodium fluoride, and dicalcium phosphate dihydrate as the abrasive, show essentially no ionic fluoride after even as low a storage period of 24 hours; and where the toothpaste contains stannous fluoride, and calcium pyrophosphate as the abrasive, there is commonly an approximately 50% loss of ionic fluoride over a period of about 6 months.
### TABLE I

Stability of Various Fluorides in Dentifrices of Example A

<table>
<thead>
<tr>
<th>Salt</th>
<th>% = 1000 PPM F&lt;sup&gt;-&lt;/sup&gt;</th>
<th>0</th>
<th>4</th>
<th>8</th>
<th>16</th>
<th>26</th>
<th>Storage Temp °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnF&lt;sub&gt;2&lt;/sub&gt; in</td>
<td>0.4 (1000)*</td>
<td>—</td>
<td>800</td>
<td>750</td>
<td>825</td>
<td>22</td>
<td>541</td>
</tr>
<tr>
<td>lined</td>
<td>0.9 (1000)*</td>
<td>—</td>
<td>875</td>
<td>750</td>
<td>825</td>
<td>37</td>
<td>226</td>
</tr>
<tr>
<td>Pb tubes</td>
<td>0.4 (1000)*</td>
<td>—</td>
<td>925</td>
<td>575</td>
<td>—</td>
<td>50</td>
<td>226</td>
</tr>
<tr>
<td>SnF&lt;sub&gt;2&lt;/sub&gt; plastic</td>
<td>0.4</td>
<td>903</td>
<td>890</td>
<td>873</td>
<td>903</td>
<td>50</td>
<td>226</td>
</tr>
<tr>
<td>tubes</td>
<td>0.3 (900)*</td>
<td>903</td>
<td>934</td>
<td>945</td>
<td>935</td>
<td>—</td>
<td>37</td>
</tr>
<tr>
<td>Naf</td>
<td>0.2 (900)*</td>
<td>—</td>
<td>—</td>
<td>855</td>
<td>810</td>
<td>50</td>
<td>22</td>
</tr>
<tr>
<td>ppm F&lt;sup&gt;-&lt;/sup&gt;</td>
<td>(900)*</td>
<td>—</td>
<td>765</td>
<td>675</td>
<td>37</td>
<td>—</td>
<td>22</td>
</tr>
<tr>
<td>TiF&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0.163</td>
<td>1043</td>
<td>982</td>
<td>982</td>
<td>—</td>
<td>37</td>
<td>22</td>
</tr>
<tr>
<td>KPO&lt;sub&gt;4&lt;/sub&gt;F&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.4</td>
<td>1043</td>
<td>920</td>
<td>920</td>
<td>—</td>
<td>37</td>
<td>22</td>
</tr>
<tr>
<td>ZrF&lt;sub&gt;4&lt;/sub&gt;2SnF&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.332</td>
<td>850</td>
<td>850</td>
<td>743</td>
<td>663</td>
<td>—</td>
<td>37</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;Po&lt;sub&gt;4&lt;/sub&gt;F</td>
<td>0.76</td>
<td>850</td>
<td>300</td>
<td>280</td>
<td>415</td>
<td>—</td>
<td>37</td>
</tr>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;Po&lt;sub&gt;4&lt;/sub&gt;F</td>
<td>0.962</td>
<td>889</td>
<td>898</td>
<td>852</td>
<td>—</td>
<td>—</td>
<td>37</td>
</tr>
</tbody>
</table>

*Initial value based on formula; not determined by analytical method.

It is generally recognized that ionically stable fluoride in dentifrices acts to make tooth enamel more resistant to attack by acids. Tests were run in vitro with illustrative toothpastes of the present invention and enamel solubilities were determined by a composite procedure based upon those reported by Rae & Clegg, J. Dent. Res. 24, 235-7 (1945); Suess & Fosdick, J. Dent. Res. 30, 177-81 (1951); Muhele et al., J. Dent. Res. 29, 182-193 (1950). The method used for preparing powdered tooth enamel was reported by Manly & Hodge and is based on a flotation process which separates the heavier enamel material from the dentin and other debris. In essence, powdered tooth enamel is exposed to a lactate buffer and the amount of dissolved calcium and/or phosphorus measured quantitatively. The percent reduction in enamel solubility is calculated from the difference between calcium and/or phosphorus dissolved from a treated sample compared to that from an untreated sample. Treatment consists of exposing 100 mg of powdered enamel to a slurry of 3 ml of water and 3 g of fluoride dentifrice for 10 minutes. The treated enamel is separated from the dentifrice materials and exposed to a lactate buffer.

In the following Table II, the results of such tests are shown using a toothpaste made according to Example A, employing stannous fluoride. All numbers, with the exception of 7.5 for the toothpaste base, are significantly different from the control values. The 44 week sample at 37°C, containing 0.4% stannous fluoride, shows an excellent reduction of 25% in enamel solubility; the 8 week sample at 50°C, containing 0.4% stannous fluoride, which usually corresponds generally to one year room temperature stability, shows an excellent reduction of 38% in enamel solubility.

### TABLE II

Enamel Solubility Reduction

<table>
<thead>
<tr>
<th></th>
<th>% P × 10&lt;sup&gt;-2&lt;/sup&gt;</th>
<th>% Ca × 10&lt;sup&gt;-2&lt;/sup&gt;</th>
<th>Average % Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control - Untreated Enamel Powder Dentifrice Base Without F&lt;sup&gt;-&lt;/sup&gt; *</td>
<td>6.02</td>
<td>12.48</td>
<td>0</td>
</tr>
<tr>
<td>0.4% SnF&lt;sub&gt;2&lt;/sub&gt; Solution = 1000 ppm F&lt;sup&gt;-&lt;/sup&gt;</td>
<td>5.57</td>
<td>11.58</td>
<td>7.5</td>
</tr>
<tr>
<td>0.2% SnF&lt;sub&gt;2&lt;/sub&gt; Solution = 500 ppm F&lt;sup&gt;-&lt;/sup&gt;</td>
<td>4.85</td>
<td>10.05</td>
<td>19</td>
</tr>
<tr>
<td>PEG Dentifrice + 0.4% SnF&lt;sub&gt;2&lt;/sub&gt;</td>
<td>5.02</td>
<td>10.35</td>
<td>17</td>
</tr>
<tr>
<td>Aged 8 wks, 22°C PEG Dentifrice + 0.4% SnF&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3.68</td>
<td>7.31</td>
<td>40</td>
</tr>
<tr>
<td>Aged 8 wks, 50°C PEG Dentifrice + 0.4% SnF&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3.77</td>
<td>7.60</td>
<td>38</td>
</tr>
</tbody>
</table>

* Diluted 50% with H<sub>2</sub>O solution for treatment.

As indicated above, the toothpastes of the present invention possess the advantage of maintaining to a substantial extent, over prolonged periods of time, fluoride ion activity, and, in their particularly advantageous, though limited, embodiments, the additional advantage of improved cleaning and polishing properties. The latter advantage is evidenced by comparisons of toothpastes using low RDA value mild abrasives, for instance, 125 to 175, with conventional commercial toothpastes using high RDA value strong abrasives, for instance, 500 to 600, in which case the average cleaning scores of the toothpastes of the present invention are at least as good as, and the strain-removing properties are superior to, those which used the high RDA value abrasives.
It heretofore has been known to prepare and commercially market toothpastes containing, in addition to (a) a major proportion of an abrasive, based on the weight of the dry ingredients of the toothpaste, (b) liquid ingredients comprising a humectant, and a substantial amount of water, generally of the order of about 40 to 45%, and also containing about 11% of a polyoxyethylene glycol of a molecular weight of the order of about 400, said percentages being by weight of the (b) or liquid phase of the toothpaste (about 5.5% by weight of the toothpaste). The apparent function of the polyoxyethylene glycol in the foregoing known toothpastes is to assist in solubilizing the flavor constituents used in the toothpaste formulation. In any event, such proportions of polyoxyethylene glycol are ineffective to achieve a cleaning enhancement or polishing effect on the teeth and, as stated above, a minimum of almost twice that quantity is required. Indeed, it is particularly advantageous, in the practice of the present invention, as has been pointed out above, that the polyoxyethylene glycol constitute from about 30 to 60% of the total weight of the liquid ingredients of the toothpaste. Moreover, such prior practice does not deal with and provides no teaching of the stabilization of fluoride-containing compounds in the presence of abrasive or polishing agents.

It has also heretofore been known, as shown in U.S. Pat. No. 2,501,145, to produce nonaqueous toothpastes containing perborate which, in use, in the presence of water, release oxygen. To increase the stability of said toothpastes against premature release of oxygen, aldehydic inactivating agents and polyoxyethylene glycols of a molecular weight in the range of 300 to 2,000 are included in the toothpaste compositions, polyoxyethylene glycols of viscous character being included to provide a suitable base for the toothpaste. Furthermore, it has been known, as shown in U.S. Pat. No. 3,250,680, to produce nonaqueous toothpastes of the self-heating type containing finely divided solid adsorbent materials capable of adsorbing water exothermically, such as silica gel, and a liquid nonaqueous vehicle which is inert to said adsorbent particles, such as polyoxyethylene glycols and polyoxypropylene glycols which melt at temperatures no higher than 75°C, such vehicles being employed in small proportions in the toothpaste, generally of the order of less than 3%. These prior known disclosures provide no teaching nor suggestion of the present invention.

It has, furthermore, heretofore been disclosed, as shown in U.S. Pat. No. 3,574,824, to prepare amorphous toothpastes containing, as essential ingredients, in certain specified proportions, certain oils of defined viscosity, such oils being mineral oils, thickened light liquid petrolatum, and vegetable triglyceride oils; a polyethylene glycol composition having a specified critical range of viscosities (about 2200 to 3400 cps at 70°F) and comprising a combination of polyethylene glycols having molecular weights ranging from about 550 to 6,000; certain non-ionic emulsifiers; certain binding agents; and mannitol and/or inositol as a compound having a negative heat of hydration; with or without such toothpaste abrasives as aluminum hydroxide, calcium sulfate, and aluminum silicate, and with or without various supplemental ingredients including, among others, enzymes, bleaching agents, and fluorides such as sodium fluoride, potassium fluoride, stannous fluoride as well as certain other fluorides. Efforts to produce toothpastes according to the disclosures in said patent, notably primary Example 1 thereof, utilizing as the toothpaste abrasive, various commercial hydrated aluminas, or a mixture of hydrated alumina and KAYPOLITE S.F., resulted in compositions which were very dry and stiff and almost impossible to extrude from tubes. When the abrasives of said Example 1 were replaced to the toothpaste abrasive dicalcium phosphate dihydrate, no paste was obtained but, rather, a dry, lumpy mixture which could not be packaged in a tube in the manner of a toothpaste and, as stated, did not constitute a paste.

The term "toothpaste", as used in the claims, will be understood to mean toothpastes which are not of the oxygen-liberating type.

What is claimed is:

1. A non-foamable toothpaste containing (a) a major proportion of a toothpaste abrasive based on the weight of the solids of said toothpaste, said abrasive consisting essentially of at least one member selected from the group consisting of precipitated calcium carbonate, dicalcium phosphate dihydrate, dicalcium phosphate anhydrous, dibasic calcium phosphate, tribasic calcium phosphate, calcium pyrophosphate, calcium sulfate, hydrated alumina and insoluble sodium metaphosphate, (b) from about 0.01% to about 0.4%, by weight of the toothpaste, of a fluoride-containing compound which is ionizable in water to yield fluoride ions, (c) at least one paste-forming ingredient, (d) at least 20%, by weight of the total of the liquid ingredients of said toothpaste, of at least one water-soluble polyoxyalkyleneglycol having an average molecular weight of at least 200, the alkylene radicals of said polyoxyalkyleneglycol containing from 2 to 4 carbon atoms, said polyoxyalkyleneglycol constituting at least about 15% by weight of the toothpaste, said toothpaste being essentially free of mineral oil, vegetable and animal triglyceride oils.

2. A toothpaste according to claim 1, wherein said toothpaste contains from about 15 to about 45% of a polyoxyalkyleneglycol by weight of said toothpaste and wherein said polyoxyalkyleneglycol is a polyoxyethylene glycol having an average molecular weight between about 650 and 670.

3. A toothpaste according to claim 1, wherein the polyoxyalkyleneglycol comprises two different polyoxyethylene glycols one of which is a normally solid polyoxyethylene glycol having an average molecular weight of about 700 and the other of which is a normally solid polyoxyalkyleneglycol having an average molecular weight of about 4000, the polyoxyalkyleneglycol 4000 being present in lesser proportions than the proportions of the polyoxyethylene glycol 700.

4. A toothpaste according to claim 1, wherein said polyoxyalkyleneglycol comprises polyoxyethylene glycols and wherein said toothpaste contains from about 35 to about 60% of polyoxyalkyleneglycol, having an average molecular weight of about 700, based on the weight of the total of the liquid ingredients of the toothpaste, and from about 5 to about 12% of a polyoxyalkyleneglycol, having an average molecular weight of about 4000, based on the weight of said toothpaste.

5. A toothpaste according to claim 1, in which the fluoride-containing compound is at least one member selected from the group consisting of sodium fluoride,
3,885,028

stannous fluoride, titanium tetrafluoride and octa-
fluorozirconotin.

6. A toothpaste according to claim 5, in which the
toothpaste abrasive is dicalcium phosphate dihydrate.

7. A toothpaste according to claim 1, which includes
an aluminum soap of a fat-forming fatty acid.

8. A toothpaste according to claim 7 in which the po-
yoxyalkyleneglycol is a normally solid polyoxyethyl-
eenglycol having an average molecular weight of about
700.

9. A toothpaste according to claim 8, which contains
aluminum stearate.

10. A non-foamable toothpaste having an RDA value
of not more than 200 and containing (a) a major pro-
portion of a mild toothpaste abrasive based on the
weight of the solids of said toothpaste, said abrasive
consisting essentially of at least one member selected
from the group consisting of precipitated calcium car-
bonate, dicalcium phosphate dihydrate, dicalcium
phosphate anhydrous, dibasic calcium phosphate, tri-
basic calcium phosphate, calcium pyrophosphate, cal-
cium sulfate, hydrated alumina and insoluble sodium
metaphosphate, (b) from about 0.01% to about 0.4%,
by weight of the toothpaste, of a fluorine-containing
compound which is ionizable in water to yield fluo-
rine ions, (c) at least one paste-forming ingredient, and (d)
at least 20%, by weight of the total of the liquid ingredi-
ents of said toothpaste, of at least one water-soluble po-
yoxyalkyleneglycol having an average molecular
weight of at least 200, the alkylene radicals of said po-
yoxyalkyleneglycol containing from 2 to 4 carbon
atoms, said polyoxyalkyleneglycol constituting at least
about 15% by weight of the toothpaste, said toothpaste
being essentially free of mineral oil, vegetable and ani-
mal triglyceride oils.

11. A toothpaste according to claim 10, wherein said
polyoxyalkyleneglycol is a polyoxyethyleneglycol and
wherein said toothpaste contains from about 15 to
about 45% of said polyoxyethyleneglycol by weight of
said toothpaste, said polyoxyethyleneglycol having an
average molecular weight between about 650 and 750.

12. A toothpaste according to claim 10, wherein the
polyoxyalkyleneglycol comprises two different poly-
oxyethyleneglycols one of which is a normally solid
polyoxyethyleneglycol having an average molecular
weight of about 700 and the other of which is a nor-
mally solid polyoxyethyleneglycol having an average
molecular weight of about 4000, the polyoxyethy-
leneglycol 4000 being present in lesser proportions than
the proportions of the polyoxyethyleneglycol 700.

13. A toothpaste according to claim 10, which in-
cludes an aluminum soap of a fat-forming fatty acid.

14. A toothpaste according to claim 13, wherein said
polyoxyalkyleneglycol comprises polyoxyethylen-
eglycols and wherein said toothpaste contains from
about 30 to about 60% of a polyoxyethyleneglycol,
having an average molecular weight of about 700,
based on the weight of the total of the liquid ingredi-
ents of the toothpaste, and from about 5 to about 12% of a
polyoxyethyleneglycol, having an average molecular
weight of about 4000, based on the weight of said
toothpaste.

15. A toothpaste according to claim 10, in which the
fluorine-containing compound is at least one member
selected from the group consisting of sodium fluoride,
stannous fluoride, titanium tetrafluoride and octa-
fluorozirconotin.

16. A toothpaste according to claim 15, in which the
toothpaste abrasive is dicalcium phosphate dihydrate.

17. A toothpaste according to claim 10 in which the
polyoxyalkyleneglycol is a polyoxyethyleneglycol and
wherein said toothpaste contains about 20% to 30% by
weight of said polyoxyethyleneglycol, said polyoxyeth-
leneglycol having an average molecular weight of
about 700.

18. A toothpaste according to claim 17, which con-
tains aluminum stearate.

19. A toothpaste according to claim 17, in which the
RDA value of said toothpaste is between about 90 and
150.

20. A toothpaste according to claim 19, in which the
fluorine-containing compound is at least one member
selected from the group consisting of sodium fluoride,
stannous fluoride, titanium tetrafluoride and octa-
fluorozirconotin.

21. A toothpaste according to claim 20, in which the
toothpaste abrasive is dicalcium phosphate dihydrate.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,885,028 - Dated May 20, 1975

Inventor(s) John A. Cella et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

The term of this patent subsequent to November 21, 1989, has been disclaimed.

Signed and Sealed this Thirteenth Day of July 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks