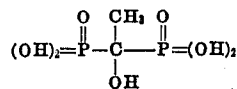


[11] 3,608,067

[56]	References Cited		
	UNITED STATES PATENTS		
3,029,191	4/1962	King	424/52
3,227,618	1/1966	Manahan et al.	424/52
3,442,604	5/1969	Smith et al.	424/57
3,488,419	1/1970	McCune et al.	424/52
<i>Primary Examiner—Richard L. Huff</i>			
<i>Attorneys—Richard W. Sternberg, Roger R. Jones and James J. Mullen</i>			

ABSTRACT: Dentifrice composition containing as the primary polishing agent a substantially water-insoluble salt of an alkylene phosphonic acid such as the calcium salt of an alkylene diphosphonic acid having the formula, e.g.



DENTIFRICE COMPOSITIONS CONTAINING INSOLUBLE SALTS OF ALKYLENE PHOSPHONIC ACIDS

The present invention generally relates to dentifrice compositions containing novel polishing agents and more particularly relates to improved dentifrice compositions containing such novel polishing agents along with stannous tin and fluoride in an ionized state. The present invention further relates to dentifrice compositions containing, as an abrasive therein, a novel ingredient which is compatible with the aforementioned stannous tin and fluoride ions which also may be present in said compositions. The present invention is more specifically directed to dentifrice compositions containing the aforementioned novel ingredient which has a polishing and cleansing effect and is further characterized, when said composition is used in oral hygiene, from deleterious abrasive or scratching action of tooth enamel and dentin.

In the field of oral hygiene, a satisfactory dentifrice should have a cosmetic effect on the teeth whereby the daily use of said dentifrice keeps said teeth in an essentially stain-free (or white-appearing) state. Such a dentifrice should also have a functional effect on the teeth and mouth, keeping them clean and free from food debris, thereby aiding the prevention of tooth decay. In order to achieve these aforementioned end results, it is generally necessary to brush the teeth with a dentifrice composition containing a cleaning agent which is generally referred to in the art as an abrasive. The main purpose of this cleaning agent is to aid in the removal from the tooth surface of tightly, adherent pellicle film which in many persons contains pigments which color said film (and thus the teeth) brown or yellow. Furthermore, this cleaning agent should remove this pellicle film with a minimum of abrasion of the underlying tooth material. The tooth surface is covered with what is commonly known as enamel which covers much of the exposed tooth surface and is a relatively hard material which, generally speaking, is not materially affected by polishing agents. However, the softer dentin, which may be exposed by receding gums, is a major problem and concern in selecting an ideal or appropriate cleaning agent. Thus, the agent selected must be one which effects the maximum removal of the pellicle film with the minimum abrasion of the dentin.

In addition to the function of the dentifrice in maintaining oral hygiene or cleanliness, there is also merit in including an ingredient which acts specifically to reduce tooth decay. In the past 15 years, extensive laboratory and field experimentation has been stimulated by the discovery of the beneficial effect of fluoride in drinking water or topically applied to the tooth surface and has subsequently led to the development of dentifrices containing stannous fluoride and, more recently, sodium monofluorophosphate. The successful effect of these fluoride (and stannous ions in the case of stannous fluoride) containing dentifrices (which include, respectively, F^1 and PO_3F^{11001} ions in solution) in reducing the incidence of caries has been established by statistical evidence. Such effectiveness is substantiated as exemplified in the body of scientific literature hereinafter set forth, and which supports the conclusion that the use of dentifrices containing a source of fluoride ions (which term, as used herein, includes F^1 , PO_3F^{111} , and other fluoride ion complexes) reduces the rate at which dental caries are formed; note J. C. Muhler, et. al., Journal of Dental Research, Vol. 33, page 606, (1954); J. C. Muhler, et. al., Journal of the American Dental Association, Vol. 50, page 163 (1955); J. C. Muhler, et. al., Journal of Dental Research, Vol. 35, page 49 (1956); and W. A. Jordon et al., Journal of the American Dental Association, Vol. 54, page 589 (1957). It is also the opinion of some scientists that the presence of stannous ions with fluoride ions gives a more effective paste than fluoride alone; note J. C. Muhler, et al., Journal of American Dental Association, Vol. 51, page 556, (1955).

One major problem in the manufacture and widespread distribution of such dentifrices is to maintain the fluoride ions (and stannous ions when using, for example, SnF_2) over a period of months, in substantially an available form, and in such form thus be available for the treatment of the teeth in a manner heretofore set forth. The main reason for this reduc-

tion of availability of such ions is the reaction thereof with the cleaning agent, i.e. the polishing agent or abrasive ingredient, to form complexes which are nonreactive with the tooth surface.

While the prior art has generally recognized this latter problem of maintaining the fluoride ions (and stannous ions) in available form when incorporated in a dentifrice composition, there has also been a substantial need in the dentifrice art for the provision of a dentifrice which contains a cleaning agent or abrasive material having a low dentin abrasion value, and which abrasive is also compatible, i.e. does not detrimentally react with the F^1 , PO_3F^{111} , Sn^{++} , with said dentifrice composition containing the ionic anticaries agent such as stannous fluoride or sodium monofluorophosphate.

Accordingly, it is one object of the present invention to provide a dentifrice composition containing a novel polishing agent.

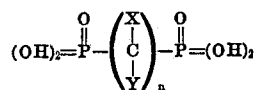
It is another object of the present invention to provide a dentifrice containing fluoride ions (and stannous ions, if using SnF_2) which do not react detrimentally with the abrasive or cleaning agent and thus remain available for treatment of the tooth surface on use.

It is another object of the present invention to provide an abrasive material which is effective in removing pellicle films from the teeth and which causes a minimum of abrasion to the tooth dentin.

Further objects and advantages of the present invention will become apparent from the subsequent description and the appended claims.

In general, the present invention provides a dentifrice composition containing ingredients usually employed in toothpowders or toothpastes and an abrasive or polishing agent comprising a substantially water-insoluble salt of an alkylene-phosphonic acid, which may be used as the sole polishing agent or in combination with minor amounts of other dental abrasives or polishing agents, such as dicalcium orthophosphate dihydrate, insoluble sodium metaphosphate, dental abrasive grade of calcium pyrophosphate and the like, and mixtures thereof.

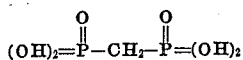
A particularly preferred class of substantially water-insoluble salts of alkylene phosphonic acids which may be employed in the dentifrice compositions are substantially water-insoluble salts of alkylene diphosphonic acids having the formula:



wherein n is an integer from 1-20 (preferably 2-10), X represents H or lower alkyl (e.g. one-four carbon atoms) and Y represents H, OH or lower alkyl (e.g. one-four carbon atoms). The most suitable salts of these acids for use in the dentifrice compositions of this invention are the calcium, barium, magnesium, zinc and/or aluminum salts, and these include partial salts, that is, those partial salts in which one or more of the hydrogen atoms of the (OH) groups in the acids of the above formula have not been replaced by such metal atoms, but which partial salts are still sufficiently insoluble in water to have utility as polishing agents in the dentifrice compositions, and also include salts in which one or more of the hydrogen atoms of the (OH) group in the acids of the above formula have been replaced by sodium or ammonium ions, but are still insufficiently insoluble in water to have utility as polishing agents in the dentifrice compositions. Also included are the hydrates of such salts. Acids of the above formula may be prepared by procedures described in U.S. Pat. No. 3,297,578 issued to Marvin M. Crutchfield and Riyad R. Irani.

Some specific examples of the aforescribed general class of substantially water-insoluble salts of alkylene diphosphonic acids are the following:

1. Calcium or magnesium salts of methylene diphosphonic acid -



specifically $CaH_2CH(PO_3)_2$ and $MgH_2CH_2(PO_3)_2$, and hydrates thereof;

2. Calcium or magnesium salts of 1-hydroxy propylidene diphosphonic acid - $(OH)_2(O)PC(OH)(CH_2-CH_3)P(O)(OH)_2$, specifically $CaH_2C(OH)(CH_2-CH_3)(PO_3)_2$ or $MgH_2C(OH)(CH_2-CH_3)(PO_3)_2$, and hydrates thereof; and

3. Calcium or magnesium salts of hexamethylenediphosphonic acid - $(OH)_2(O)PCH_2(CH_2)_4CH_2P(O)(OH)_2$, specifically $CaH_2(PO_3)CH_2(CH_2)_4CH_2C(H_2)(PO_3)$ or $MgH_2(PO_3)CH_2(CH_2)_4CH_2C(H_2)(PO_3)$, and hydrates thereof; and

4. Calcium or magnesium salts of 1-hydroxy ethylidene diphosphonic acid - $(OH)_2(O)PC(OH)(CH_3)P(O)(OH)_2$, specifically $CaH_2(PO_3)C(OH)(CH_3)(PO_3) \cdot H_2O$ or $MgH_2(PO_3)C(OH)(CH_3)(PO_3) \cdot 2H_2O$ or the corresponding anhydrous salts or different hydrates of such salts.

Another embodiment of the present invention provides a dentifrice composition containing (a) one or more of the aforedescribed substantially water-insoluble salts of the alkylene phosphonic acids; and (b) a water-soluble, innocuous (as hereinafter defined), fluoride salt such as water-soluble, fluorine-containing organic salts; water-soluble fluorine-containing inorganic salts, and mixtures thereof. If desired, a water-soluble, innocuous, stannous tin salt of a mineral acid may be added to the above-described composition in order to provide stannous ions (if SnF_2 is not the fluoride salt) or an excess of stannous ions (even if SnF_2 is used). It is to be noted that the fluorides included under item (B) and said tin salt can represent either the same compound, for example, stannous fluoride, or different compounds, for example, (b) can be sodium fluoride and such additional stannous tin salt can be stannous fluoride.

The adjective "innocuous," as used herein in regard to fluoride and stannous compounds means a compound which is substantially nontoxic in the proportions used, or is not highly colored, or is not otherwise objectionable for use in a dentifrice composition.

The substantially water-insoluble salts of alkylene phosphonic acids have a satisfactory degree of polishing and cleansing action and at the same time they are sufficiently nonabrasive to minimize scratching or other deleterious effects on the enamel or cementum of the teeth. Such salts usually have a dentin abrasion value, as hereinafter defined, of less than 500, usually from 200 to about 350. A polishing agent having this low dentin abrasion value is still effective in its cleansing action when applied in oral hygiene but, on the other hand it does not detrimentally abrade the tooth surface. Dicalcium orthophosphate dihydrate, a commonly used polishing agent in dentifrices, usually has a dentin abrasion value of about 250-350.

The dentin abrasion value is a relative number indicating the degree of abrasiveness of a material. The procedure for the evaluation of this abrasiveness is the method of Grabenstetter et al. described in the Journal of Dental Research, Vol. 17, No. 6, Nov.-Dec. 1958, pages 1,060-1,068; note also U.S. Pat. No. 2,876,168. Briefly, the cleaning agent or abrasive is determined to have a certain dentin abrasion value after it has been utilized in the mechanical brushing of radioactive dentin from extracted human teeth.

In general, the aforementioned substantially water-insoluble salts of alkylene phosphonic acids (as polishing agents) constitute from about 0.5 percent to about 96 percent by weight of the total weight of the dentifrice composition. When such polishing agents are being utilized in a dentifrice composition such as toothpaste, it is preferred that they be present in an amount of from about 20 percent to about 60 percent by weight of the total weight of the dentifrice composition. On the other hand, when it is desired to prepare a toothpowder, it

is preferred that such polishing agents be present in an amount of from about 60 percent to about 96 percent by weight based on the total weight of the dentifrice composition.

It is preferred that the polishing agents of this invention be in solid particulate form. If they have first been prepared in lumps or sizable particles they can be reduced to the desired particle size by conventional grinding methods such as impact, ball, and tube mills. If the polishing agents are initially prepared in the form of solid particles having the desired size distribution, a grinding step is not necessary.

It is preferred that the polishing agents of this invention be composed of solid particles substantially all of which have a diameter of less than 50 microns. Larger particles tend to feel gritty in the mouth and to stick between teeth. The mean diameter of the particles of the polishing agents is desirably between about 5 microns to about 40 microns and preferably from about 5 microns to about 20 microns, for optimum performance. Preferably not more than about 10 weight percent of the particles have a diameter of less than about 1 micron. Finer particles are relatively ineffective in cleaning teeth, and therefore the fraction of finer particles should be limited. By particle is meant aggregates as well as individual particles. It might be supposed that only particles with sharp edges and corners would be effective in removing pellicle film from the teeth. However, it has been discovered that relatively spherical particles and aggregates of relatively spherical particles also serve as effective cleaning agents. (The particle diameters referred to herein were determined by microscopic measurements using a calibrated eyepiece.)

In the case of fluoride-containing dentifrice compositions the fluoride ions are usually incorporated in the dentifrice composition in the form of stannous fluoride which also provides stannous tin ions (in solution). However, when it is desirable to control the ratio of stannous ions to fluoride ions, such control being suggested by the prior art (for example, note U.S. Pat. No. 2,946,725), in order to provide more stannous ions than the fluoride ions available in stannous fluoride, the stannous tin can be supplied in the form of a water-soluble, stannous tin salt of a mineral acid (hereinafter referred to as the other stannous salt). As examples of such other stannous tin salts, there may be mentioned, for exemplary purposes only, compounds such as stannous chloride, stannous sulfate, stannous nitrate, monochlorostannous fluoride (Sn_2ClF_3 and $SnClF$), fluorostannites — for example, $KsnF_3$, hexafluorozirconate — for example, $SnZrF_6$, and the like.

The other stannous salt content of the dentifrice composition, as expressed in parts per million of the stannous ions, should be in the range of from about 2,000 to about 15,000 parts of stannous ion per million parts of the total weight of such dentifrice composition. It is generally preferred that the stannous ion be present, when used in such composition, in the range of from about 6,000 to about 11,000 parts per million stannous tin. Especially effective dentifrices are usually obtained when the minimum total stannous tin content is about 6,000 parts per million to about 8,000 parts per million. Experimental evidence indicates that if the stannous tin content is below the lower limit of 2,000 parts per million the dentifrice compositions tend to lose some of their effectiveness in regard to caries prevention. Furthermore, when the tin content is above about 15,000 parts per million, no further solubility reduction of the tooth enamel is apparent.

Fluoride ions may be incorporated in the dentifrice compositions of this invention by the incorporation of any one or mixtures of water-soluble, innocuous, fluorine-containing organic or inorganic salts. Many water-soluble inorganic fluoride salts are suitable sources of fluoride ions, i.e. F^- or complex fluoride ions, e.g. PO_3F^{111} . Among these salts there may be mentioned, for exemplary purposes only, NaF , PbG_2 , FeF_2 , LiF , CaF_2 , NaF , KF , NH_4F , PdF_2 and the like. It should also be understood that the term "fluoride salts," as used herein, is also intended to include complex water-soluble fluoride-containing salts such as fluorophosphates, e.g. Na_2PO_3F , fluorosilicates, e.g. Na_2SiF_6 and H_2SiF_6 , fluorizir-

conates, e.g. CaZrF_6 , Na_2ZrF_6 , K_2ZnF_6 , fluoroborates, e.g. NaBF_4 , and fluorotitanates. Mixtures of the aforementioned fluoride salts can also be used herein.

The "fluoride ion," which term includes, for example, both F^- and PO_3F^{1-} or other complex ions, may also be supplied to the dentifrice composition by means of an organic fluoride which is soluble in water or at least which dissociates to give fluoride ions when in contact with water. As examples of organic fluorides, there may be mentioned the organic hydrofluorides, i.e. amine fluorides like mono-, di-, and triethanolamine hydrofluorides, such as those compounds disclosed in Canadian Pat. 543,066 issued on July 2, 1957, to Philip Zutover et al. and which patent is incorporated herein by reference. These compounds may also be named as the corresponding ethanolammonium fluorides such as triethanolammonium fluoride. Other useful organic fluorides and hydrofluorides are disclosed in a publication by H. R. Muhlemann et al. in *Helvetica Odontologica*, Vol. I, No. 2, page 23, 1957, which publication is also incorporated herein by reference.

The quantity of the water-soluble fluoride compounds, which may be used in combination with stannous tin in the dentifrice compositions of this invention, should be an amount equivalent to provide at least 25 parts of fluoride ions per million parts of the total dentifrice composition. It has been found that extremely large amounts of fluoride ions do not appreciably enhance the desirable properties of the dentifrice and may, under certain circumstances, produce toxic effects. Accordingly, it is desirable that the dentifrices of the present invention contain not more than a total of about 4,000–5,000 parts of ionized and un-ionized fluorine per million parts of dentifrice composition and preferably not more than 3,000 p.p.m. However, a level of from about 1,000 to about 10,000 p.p.m. fluoride ions can be used, if desired, without toxic effects. A preferred level of fluoride ions is from about 500 p.p.m. to about 2,000 per million parts of the total dentifrice composition. (It is to be noted that when the fluoride salt is, for example, sodium monofluorophosphate, $\text{Na}_2\text{PO}_3\text{F}$, it has previously been found that it is not necessary to utilize a stannous tin salt, i.e. to supply Sn^{++} , in order to obtain an effective anticaries dentifrice.)

While the foregoing description has been directed primarily to various ways of incorporating stannous tin ions and fluoride ions in a dentifrice composition, it is also possible, as previously mentioned, to use stannous fluoride per se as the source of stannous and fluoride ions. Stannous fluoride generally is used in amounts less than 50,000 parts per million by weight, based on the total weight of the dentifrice composition. It is preferred that this salt, i.e. SnF_2 , level be less than 25,000 p.p.m. and between the range of from about 200 p.p.m. and 2,000 p.p.m. by weight.

Generally the major portion of ingredients (i.e. in excess of 50 percent by weight) of a dentifrice composition comprise the polishing agent or the polishing agent and fluoride compound.

It is desirable that the pH of the dentifrice composition of this invention lie between about 5 and about 8, preferably from about 5 to about 7, and more desirably from about 5.5 to about 6.5. When the pH of the dentifrice composition is above about pH 8, there results a loss of metal ions, i.e. stannous ions, available for reaction with enamel and, in addition, certain flavoring substances, especially esters, deteriorate rapidly. At a pH below about 4 or 5, there is produced an astringent paste which is generally objectionable to most people. In addition, the lower pH also accelerates the hydrolysis of certain of the sudsing agents normally used in dentifrices thereby producing an unpleasant "fatty acid taste" and reducing the amount of sudsing obtained. Furthermore, when the pH values are below 4 or 5, there is a tendency to cause corrosion of metal tubes in which the paste is stored and also there is a tendency to hydrolyze other ingredients in the dentifrice mixture. It should be noted that when referring to pH herein, the pH values specified are those obtained by measuring the

pH of the supernatant liquid resulting by forming a slurry of 1 part by weight of dentifrice and 3 parts by weight distilled water.

In addition to the aforementioned ingredients utilized in the dentifrice compositions of the present invention, such compositions may also conventionally contain foaming or sudsing agents although the use of these agents is not critical in the practice of the present invention. Any of the commonly used foaming or sudsing agents can be used if they are reasonably stable, nontoxic and foam or form suds within the pH range of the dentifrice of this invention. As examples of suitable sudsing agents, there may be mentioned water soluble alkyl and alkyl ether sulfates and sulfonates having alkyl groups of from about light to about 18 carbon atoms, water-soluble salts of sulfonates, monoglycerides of fatty acids having from about 10 to about 18 carbon atoms, water-soluble salts of sulfated fatty alcohols having from about 10 to about 18 carbon atoms, salts of fatty acid amides of taurines such as sodium-N-methyl-N-palmitoyl tauride, salts of fatty acid esters of isethionic acid, and salts of substantially saturated aliphatic acyl amides of saturated aliphatic monoaminocarboxylic acids having from about two to about six carbon atoms and in which the acyl radical contains from about 12 to about 16 carbon atoms, such as sodium N-lauroyl sarcoside. It is also to be understood that mixtures of two or more sudsing agents can be utilized herein. These sudsing agents are generally used in an amount of from about 0.5 percent to about 5.0 percent by weight, based on the weight of the dentifrice composition.

In addition to the aforementioned ingredients, it may also be necessary, in order to obtain the proper consistency in certain toothpastes, to add various thickening materials. As examples of such thickening materials there may be mentioned water-soluble salts of cellulose ethers such as sodium carboxymethylcellulose and sodium carboxymethyl hydroxyethyl cellulose. Natural gums such as gum karaya, gum arabic, and gum tragacanth also can be used as thickeners but may tend to cause undesirable odors or flavors in some formulations. In addition to the above-mentioned thickeners, colloidal magnesium aluminum silicate or finely divided silica (such as silica aerogels or fume silica) can also be used as a part of the thickening agent for improvement in texture. These thickening agents are generally used in an amount of from about 0.5 percent to about 5.0 percent by weight, based on the weight of a toothpaste dentifrice composition.

The dentifrice compositions of the present invention may also include, in addition to any of the aforementioned ingredients, suitable humectants, such as glycerine, sorbitol and other polyhydric alcohols. These humectants are generally used in an amount of from about 0.5 percent to about 35 percent of the dentifrice composition.

The dentifrice compositions may also additionally contain small amounts of flavorings such as oil of wintergreen, oil of peppermint, oil of spearmint, oil of sassafras, and oil of anise. Small amounts of sweetening agents such as saccharin, dextrose, levulose, and sodium cyclamate are also conventionally added to dentifrices.

In toothpaste formulations, water is generally used as a base and is present in an amount of from about 5 percent to about 60 percent by weight, based on the total weight of the composition.

Finally, if one further desires, a suitable coloring agent may be added to said dentifrice composition in order to enhance its aesthetic effect.

All of the aforementioned ingredients which are utilized in the present invention dentifrice compositions may be incorporated therein in any order, in order to formulate said compositions.

A further understanding of the novel and unique compositions of the present invention will be obtained from the following specific examples which are intended to illustrate the invention, but not to limit the scope thereof, parts and percentages being by weight unless otherwise specified.

EXAMPLE I

A toothpaste was prepared by first grinding 800 grams of solid particles of the monocalcium salt of 1-hydroxy, 1-ethylidene diphosphonic acid as the dihydrate, that is, $\text{CaH}_2(\text{PO}_3)_2 \cdot 2\text{H}_2\text{O}$, until at least 90 percent of the particles were of a size within the range of about 1 to about 20 microns. The resulting material was the polishing agent. Next a solution was prepared by mixing together 306 grams of glycerine, 306 grams of water and 1 gram of saccharine, which solution was heated to 90° C. while thoroughly mixing the ingredients. This solution was then added with thorough mixing to the aforementioned polishing agent, and to the resultant mixture was added a solution consisting of (a) 60 milliliters of water, (b) 28 grams of sodium laurylsulfate, (c) 60 grams of glycerine and (d) 10 grams of mint flavoring. The resulting paste mixture was thoroughly mixed together until a toothpaste consistency was achieved. This paste which has a pH of about 5 was a satisfactory cleaning agent for teeth when used in the customary way with a toothbrush, and had a dentin abrasion value of about 285.

EXAMPLE II

A toothpaste was prepared using the same ingredients and procedure described in example I with the exception that a slurry of 11.8 grams of stannous fluoride in 50 milliliters of water was used instead of the 60 milliliters of water referred to under (a) in example I. The resulting paste was stored in a closed bottle for 30 days at 20° C., after which a sample was withdrawn from the bottle and analyzed for percent available fluoride in order to ascertain the compatibility, as hereinafter defined, of the polishing agent in the presence of fluoride and stannous tin ions. The available fluoride and stannous tin is that fluoride and tin which have not been hydrolyzed or oxidized and which are available for absorption by the enamel of a tooth surface.

The aforementioned fluoride ion "compatibility" was determined in the following manner. Approximately 10 grams of the toothpaste were shaken with 100 milliliters of distilled water for 1 hour at a setting of 4 (the range is from 1 to 10 with 10 being the fastest) on an automatic shaker, commercially available under the trade name Burrell shaker. The resulting slurry was then centrifuged for 15 minutes at the maximum speed in a high-speed centrifuge, commercially available under the trade name Servell centrifuge. A 25-milliliter portion of the clear supernatant liquid was transferred to a small bottle containing 4 grams of tricalcium phosphate. The bottle was capped and placed in the above-described Burrell shaker and shaken for 20 minutes at a setting of 4. The resultant tricalcium phosphate sample treated with the slurry made from the toothpaste formulation was then transferred to a Buchner funnel, filtered and washed with three 15-milliliter portions of water and then washed with three 15-milliliter portions of acetone and then finally dried in air. The sample was then analyzed for fluorine content by emission spectroscopy. The percent of compatibility, that is, the amount of fluoride ions remaining after a period of time when in contact with the aforementioned abrasives is determined in accordance with the following formula:

compatibility =

$$\frac{\text{concentration of fluoride ions after tests}}{\text{concentration of fluoride ions before tests}} \times 100$$

As a result of the above-described analytical procedure it was determined that the toothpaste after 30 day's storage had a fluoride compatibility of 31.7 percent. By way of contrast a comparable toothpaste prepared by using calcium pyrophosphate ($\text{Ca}_2\text{P}_2\text{O}_7$) as the abrasive or polishing agent had a fluoride compatibility of about 15.9 percent.

It can readily be seen then, from the aforementioned results, that the calcium salt of alkylene diphosphonic acid not only

has a low dentin abrasion value but is quite compatible with a dentifrice composition containing fluoride ions in such a composition during an extended storage period.

EXAMPLE III

The aforementioned example II of the present invention was repeated with the exception that in place of the slurry of stannous fluoride dissolved in water, there was substituted a slurry of a mixture of stannous nitrate and sodium fluoride dissolved in water. Such mixture was used in an amount to provide the same stannous and fluoride ion concentrations as obtained in example II. The results obtained were substantially the same as those results set forth in example II. Thus, the use of separate and different compounds to provide stannous and fluoride ions to the dentifrice composition yields the same abrasive compatibility results as contrasted to the utilization of stannous fluoride.

EXAMPLE IV

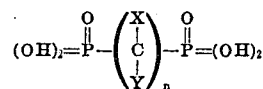
The aforementioned example II of the present invention was again repeated with the exception that in place of the slurry of stannous fluoride dissolved in water, there was substituted a mixture of sodium monofluorophosphate dissolved in water. The amount of such sodium monofluorophosphate used was sufficient to provide approximately 2,000 parts per million of fluoride ions, i.e. $\text{PO}_3\text{F}^{111}$. The results obtained were substantially the same as those results set forth in example II with reference to the available fluoride in a toothpaste mixture stored over a period of approximately 30 days. From these results showing the compatibility of sodium monofluorophosphate with the calcium salt of alkylene diphosphonic acid, it can readily be seen that this abrasive material is compatible with a wide variety of fluoride-containing water-soluble salts.

EXAMPLE V

A toothpowder was prepared by thoroughly mixing together 96 grams of the polishing agent described in example I together with 1.5 grams of powdered sodium lauryl sulfate, 1.2 grams of oil of peppermint, 1 gram of sodium citrate and 0.3 gram of saccharine. A slurry of the resulting toothpowder had a pH of about 5, and a dentin abrasion value of about 285.

What is claimed is:

1. A toothpaste composition comprising as the primary polishing agent a member selected from the group consisting of (1) a substantially water-insoluble salt selected from the group consisting of calcium salt, magnesium salt, zinc salt, aluminum salt and mixtures thereof of alkylene diphosphonic acid having the formula:



wherein n is an integer from 1 to 20, X is selected from the group consisting of H and a lower alkyl radical of one to four carbon atoms and Y is selected from the group consisting of H, OH, and a lower alkyl radical of one to four carbon atoms; and (2) a hydrate of said salts, the particles of said polishing agent having a mean diameter of from about 5 microns to about 40 microns, said polishing agent having a dentin abrasion value of less than 500, and said polishing agent being present in said dentifrice composition in an amount of from about 20 weight percent to about 60 weight percent based on the weight of the dentifrice composition.

2. A composition according to claim 1, wherein the composition is a toothpaste.

3. A dentifrice composition as set forth in claim 1 wherein said polishing agent is a salt selected from the group consisting of a calcium salt of 1-hydroxy, 1-ethylidene diphosphonic acid and a hydrate thereof.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,608,067 Dated September 21, 1971

Inventor(s) Riyard R. Irani

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

Column 3, line 5, " $\text{CH}(\text{PO}_3)_2$ " should read -- $\text{CH}_2(\text{PO}_3)_2$ --;
line 20, " $) (\text{PO}_3) \cdot \text{H}_2\text{O}$ " should read -- $) (\text{PO}_3) \cdot 2\text{H}_2\text{O}$ --.

Signed and sealed this 11th day of July 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents