DENTIFRICE COMPOSITIONS CONTAINING INSOLUBLE SALTS OF AMINO ALKYLENE PHOSPHONIC ACIDS

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3 Claims

ABSTRACT OF THE DISCLOSURE

Dentifrice compositions containing as the primary polishing agent a substantially water-insoluble salt of an amino-alkylene phosphonic acid such as the calcium salt of an amino tri(alkyldiene phosphonic acid) having the formula, e.g.

\[ \text{N}-(\text{CH}_2\text{PO}_3\text{H}_2)_3 \]

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 aminosine tin and fluoride in an ionized state. The present invention further relates to dentifrice compositions containing, as an abrasive ingredient, a novel abrasive 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 abrasive 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 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⁻ and PO₂F⁻ ions in solution) in reducing the incidence of caries has been well established by statistical evidence. Such effectiveness is substantiated as exemplified by 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⁻, PO₂F⁻, 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 present, for example, SnF₂) over a period of many months, in substantially an available form, and in such form to be available for the treatment of the teeth in a manner heretofore set forth. The main reason for this reduction 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 non-reactive with the tooth surface and which are innocuous to the surrounding soft tissues.

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 such ions in an available form and which shows a minimum abrasion value and which is non-reactive with other cleaning agents 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 SnF₂) 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 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 toothpaste dentifrices or polishing agent comprising a substantially water-insoluble salt of an aminoalkylene 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 dithiate, insoluble sodium metaphosphate, dental abrasives made of calcium pyrophosphate and the like, and mixtures thereof.

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

wherein A is a group, \( R_1 \) is H, an aliphatic radical containing from 1–20, preferably 1–4, carbon atoms, or A, and \( R_2 \) is H, an aliphatic radical containing from 1–20, preferably 1–4, carbon atoms, A or

\[
\begin{array}{c}
\text{Y} \\
\text{O} \\
\text{P} = \text{(OH)}_2 \\
\text{Y'}
\end{array}
\]

wherein \( n \) is an integer from 1 to 20 (preferably 3–10); \( Z \) is H or A and \( Z' \) is A or

\[
\begin{array}{c}
\text{Y} \\
\text{O} \\
\text{C} \\
\text{N} \\
\text{Z} \\
\text{Y'} \\
\text{Z'}
\end{array}
\]

wherein \( m \) is an integer from 1 to 20 (preferably 3–10); \( Y \) and \( Y' \) in the above formula represent straight or branched chain lower aliphatic radicals, preferably 1 to 4 carbon atoms and hydrogen, which are unsubstituted or which may be substituted with groups such as hydroxyl, halide, alkoxy, sulfanyl, carboxyl, amide or amino groups; and either \( R_1 \) or \( R_2 \) have at least one group corresponding to A. 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 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 hydrogen atoms of the (OH) groups in the above formula have been replaced by sodium or ammonium ions, but are still sufficiently insoluble in water to have utility as polishing agents in the dentifrice compositions. Also included are hydrates of such salts. Acids of the above structural formula may be prepared by the procedures described in U.S. Pat. No. 3,298,956, issued to Riyad R. Irani and Kurt Moedritzer on Jan. 17, 1967. Some specific examples of the aforementioned general class of substantially water-insoluble salts of amino-alkylene phosphonic acids are the following:

1. Calcium or magnesium salts of aminotrimethylene phosphonic acid-

\[
\text{Ca}_2\text{H}_2\text{N(CH}_2\text{PO}_3\text{)}_2\text{HN(CH}_2\text{PO}_3\text{)}_2\text{H}_2\text{O}
\]

specifically \( \text{Ca}_2\text{H}_2\text{N(CH}_2\text{PO}_3\text{)}_2\text{HN(CH}_2\text{PO}_3\text{)}_2\text{H}_2\text{O} \)

where \( X \) may vary from 1 to 7;

\[
\text{Mg}_2\text{H}_2\text{N(CH}_2\text{PO}_3\text{)}_2\text{HN(CH}_2\text{PO}_3\text{)}_2\text{H}_2\text{O}
\]

where \( X \) may vary from 4 to 10; and

2. Calcium or magnesium salts of hexamethylene diamine tetra(methylphosphonic acid)-

\[
[\text{CH}_2\text{PO(OH)}_2\text{HN(CH}_2\text{PO}_3\text{)}_2\text{HN(CH}_2\text{PO}_3\text{)}_2\text{OH}]_2
\]

specifically \( \text{Ca}_2\text{H}_2\text{N(CH}_2\text{PO}_3\text{)}_2\text{HN(CH}_2\text{PO}_3\text{)}_2\text{N(CH}_2\text{PO}_3\text{)}_2\text{HN(CH}_2\text{PO}_3\text{)}_2\text{H}_2\text{O} \) and hydrates thereof; and

(3) Calcium or magnesium salts of amino di(methylphosphonic acid) (butylidene phosphonic acid)-

\[
\text{N}[\text{CH}_2\text{PO(OH)}_2\text{HN(CH}_2\text{PO}_3\text{)}_2\text{HN(CH}_2\text{PO}_3\text{)}_2\text{H}_2\text{O}]
\]

specifically \( \text{Ca}_2\text{H}_2\text{N(CH}_2\text{PO}_3\text{)}_2\text{HN(CH}_2\text{PO}_3\text{)}_2\text{N(CH}_2\text{PO}_3\text{)}_2\text{HN(CH}_2\text{PO}_3\text{)}_2\text{H}_2\text{O} \) and hydrates thereof.

Another embodiment of the present invention provides a dentifrice composition containing (a) one or more of the aforementioned substantially water-insoluble salts of the aminoalkylene phosphonic acids; and (b) a water-soluble, innocuous (as far as harm or duress is concerned) salt, such as water-soluble, fluoride-containing organic salts; water-soluble fluoride-containing inorganic salts; and mixtures thereof. If desired, a water-soluble, innocuous, stannous tin salt of a mineral acid can be added to the above-described composition, in order to provide stannous ions (if SnF₂ is not the fluoride salt) or an excess of stannous ions (even if SnF₂ is used). It is to be noted that the fluorides included under (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 non-toxic in the proportions used, or not highly colored, or otherwise objectionable for use in a dentifrice composition. The substantially water-soluble salts of amino-alkylene phosphonic acids have a satisfactory degree of polishing and cleaning action and at the same time they are sufficiently non-abrasive to minimize scratching or other deleterious effects on the enamel or cementum of the teeth. Such salts usually have a dentin abrasion value of about 1000, 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 cleaning 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 Grabensteen et al., described in the Journal of Dental Research, Vol. 17, No. 6, November-December 1958, pp. 1060–1068; 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 amine alkylene phosphonic acids (as polishing agents) constitute from about 0.5% to about 96% 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% to about 60% 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% to about 96% 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 preferably 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 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 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 patent art (for example, U.S. Patent 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 tin 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 (SnClF2 and SnClF4), fluorostannates—for example, KSnF3, hexafluorosilicate—for example, SnF62−, 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 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 in 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, fluoride-containing organic or inorganic salts. Many water-soluble inorganic fluoride salts are suitable sources of fluoride ions, e.g., F− or complex fluoride ions, e.g., PO4F2−. Among these salts there may be mentioned, for exemplary purposes only, InF3, PbF2, FeF2, LiF, CaF2, NaF, KF, NH4F, PdF2 and the like. It should also be understood that the term "fluoride salts," as used herein, also includes any complex water-soluble fluoride-containing salts such as fluorophosphates, e.g., NaPO4F2, fluorosilicates, e.g., Na2SiF6 and H2SiF6, fluorozirconates, e.g., CaZrF6, Na2ZrF6, K2ZrF6, fluoroborates, e.g., NaBF4, and fluorotitanates. Mixtures of the aforementioned fluoride salts can also be used herein.

The "fluoride ion," which term includes, for example, both F− and PO4F2− 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 fluoroacetates such as those compounds disclosed in Canadian Patent 543,066 issued on July 2, 1957, to Philip Zutavern et al. and which patent is incorporated herein by reference. These compounds may also be named as the corresponding ethanol-ammonium fluorides such as triethanolammonium fluoride. Other useful organic fluorides are disclosed in a publication by H. R. Mahle mann 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 unionized fluoride per million parts of dentifrice composition and preferably not more than 3,000 p.p.m. However, a level of from about 1000 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, Na2PO4F, it has previously been found that it is not necessary to utilize a stannous fluoride to supply Sn++, in order to obtain an effective antacaries 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., SnF2, 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% by weight) of a dentifrice composition comprises 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 taste which is generally objectionable to most people. In addition, the lower pH also accelerates the hydrolysis of certain of the sudsing agents and surfactants 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
A toothpaste was prepared by first grinding 800 grams of solid particles of the dicalcium salt of amino-trimethylphosphinic acid as the hydraphosphate, that is, Ca$_2$H$_2$N(CH$_3$)$_2$PO$_4$·H$_2$O, until at least 90% 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 saccharin, which solution was heated to 50° C. While thoroughly and individually the ingredients of Example I were 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 glycérine and (d) 10 grams of mint flavoring. The resulting paste mixture was thoroughly mixed together until a toothpaste consistency was achieved. This paste which had a pH of about 6 was a satisfactory cleaning agent for teeth when used in the customary way with a toothbrush, and had a dentin abrasion value of about 300.

**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 and stannous ions to ascertain the compatibility, as hereinafter defined, of the polishing agent in the presence of fluoride and stannous ions. The available fluoride and stannous ion 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 and stannous ion "compatibility" was determined in the following manner. Approximately 10 grams of the toothpaste were shaken with 100 milliliters of distilled water for one 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 acetone and then finally dried in air. The sample was then analyzed for fluoride and stannous ion content by emission spectroscopy. The percent of compatibility, that is, the amount of fluoride and stannous ions remaining after a period of time when in contact with the aforementioned abrasives is determined in accordance with the following formula:

\[
\text{Compatibility} = \frac{\text{concentration of stannous or fluoride ions after tests}}{\text{concentration of stannous or fluoride ions before tests}} \times 100
\]

As a result of the above-described analytical procedure it was determined that the toothpaste after 30 days storage had a fluoride compatibility of 33.5% and stannous ion compatibility of 27.2%. By way of contrast a comparable
toothpaste prepared by using calcium pyrophosphate (Ca$_2$P$_2$O$_7$) as the abrasive or polishing agent had a fluoride compatibility of about 15.9% and a stannous ion compatibility of about 16%.

It can readily be seen, from the aforementioned results, that the calcium salt of amino alkylene phosphonic acid not only has a low dentin abrasion value but is quite compatible with a dentifrice composition containing fluoride and stannous 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 ion, i.e., PO$_4^{3-}$. 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 amino alkylene phosphonic 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 saccharin. A slurry of the resulting toothpowder had a pH of about 6, and a dentin abrasion value of about 300.

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 a calcium salt, magnesium salt, zinc salt, aluminum salts and mixtures thereof of an amino alkylene phosphonic acid having the formula: 

   $\begin{align*}
   &\text{R}_1 \\
   &\text{R}_2 \\
   &\text{N} \quad \text{A} \\
   &\text{Y} \\
   &\text{O} \\
   &\text{P}=(\text{OH})_2 \\
   &\text{Y}
   \end{align*}$

   wherein A is a group, R$_1$ is selected from the group consisting of H, an aliphatic radical containing from 1 to 4 carbon atoms, and A, and R$_2$ is selected from the group consisting of H, an aliphatic radical containing from 1 to 4 carbon atoms, A, and

   $\begin{align*}
   &\text{Y} \\
   &\text{N} \quad \text{Z} \\
   &\text{Y} \\
   &\text{Y} \\
   &\text{O} \\
   &\text{P}=(\text{OH})_3 \\
   &\text{Y}
   \end{align*}$

   wherein n is an integer from 3 to 10; Z is selected from the group consisting of H and A, and Z' is selected from the group consisting of A and

   $\begin{align*}
   &\text{Y} \\
   &\text{Z} \\
   &\text{Y} \\
   &\text{Y} \\
   &\text{O} \\
   &\text{P}=(\text{OH})_3 \\
   &\text{Y}
   \end{align*}$

   wherein m is an integer from 3 to 10; Y and Y' are selected from the group consisting of straight chain aliphatic radicals having from 1 to 4 carbon atoms, branched chain alkylene radicals having from 1 to 4 carbon atoms and H, 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 dentifrice composition as set forth in 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 amino(trimethylene phosphonic) acid and a hydrate thereof.

References Cited

UNITED STATES PATENTS

3,029,191 4/1962 King 424—52
3,227,618 1/1966 Manahan et al. 424—52

RICHARD L. HUFF, Primary Examiner

U.S. Cl. X.R.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,642,979
DATED : February 15, 1972
INVENTOR(S) : Riyad 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 4, line 33, "water-soluble" should be corrected to read -- water-insoluble --.

Signed and Sealed this
Twenty-first Day of March 1978

[SEAL]

Attest:

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