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3,269,814

DENTIFRICE POLISHING AGENTS

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This application is a continuation-in-part of our co-pending application, Serial No. 83,938, filed January 23, 1961, now abandoned.

The present invention is directed to intimate mixtures of condensed phosphates suitable as dentifrice polishing agents in formulations designed for application of active fluorides to the teeth, and their method of manufacture.

In recent years, considerable effort has been devoted to evaluating and perfecting the means for applying soluble fluorides to human teeth. It is now generally recognized that the fluoride ion (supplied from a soluble fluoride salt such as SnF_2 or NaF) tends to lessen or minimize dental caries when applied either topically to the teeth from a concentrated solution or paste, or when incorporated in municipal drinking water.

Nevertheless, the use of soluble fluorides in toothpastes or toothpowders gives rise to a problem of compatibility. Briefly, it is difficult to prepare a polishing agent ingredient for toothpastes or powders which, when combined in a formulation together with a fluoride, will not react with the fluoride and diminish its effectiveness as a decay preventative. In fact, most of the conventional polishing agents used for many years in non-fluoride pastes and powders will substantially inactivate the fluoride ion making it unavailable for later reaction at the outer layers of human teeth, i.e., with the hydroxylapatite component of tooth enamel and dentin.

Most of the major fluoride dentifrice formulators have heretofore selected polishing ingredients from among the well-known fairly insoluble phosphates and polyphosphates, primarily calcium pyrophosphate (see, e.g., U.S. Patent 2,876,166) and insoluble sodium metaphosphate, in an effort to achieve the highest degree of compatibility possible with commercially available materials.

It is also generally recognized that the tin (II) ion, when supplied from stannous fluoride, is effective in reducing tooth decay. Recent studies have revealed that the stannous or tin (II) ion reacts, like fluoride ion, at the surface or slightly within tooth enamel to form a complex tin compound, probably tin (II) hydroxyorthophosphate, see, e.g., Journal of Dental Research, vol. 4, No. 6, Nov.—Dec. 1961, pp. 1199—1210, and that erupted human teeth are deficient in tin in the outermost layers, containing virtually none in deeper layers, *ibid*, p. 1200.

But again, like the fluoride ion, tin (II) tends to react when combined with other chemical ingredients, thereby becoming inactivated or unavailable when applied to the teeth. It is therefore obvious that stannous fluoride, probably the most effective of the present day fluoride decay preventatives, must be utilized in a compatible medium if it is to be effective at the time of topical application to the teeth. When it is applied from a toothpaste, the polishing agent ingredient therein must be unreactive, the degree of compatibility being a quantitative measurement of the suitability of the polishing agent for use with tin (II)-containing formulations.

It is an object of this invention to furnish improved inorganic phosphate dentifrice polishing agents.

Another object of this invention is to furnish inorganic phosphate dentifrice polishing agents which, when included in a fluoride-containing dentifrice preparation, will permit a large percentage of the originally added fluoride constituent to remain in an available, ionized state.

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A further object of this invention is to furnish inorganic phosphate dentifrice polishing agents which, when included in a tin fluoride-containing dentifrice preparation, will permit a large percentage of both the tin and the fluoride ions to remain in an available, ionized state.

Still another object of this invention is to furnish a method by which the fluoride-compatible phosphates of the invention may be manufactured.

Other objects will readily appear to those familiar with the art as the description proceeds.

We have now discovered that the addition of an acidic phosphate, or a phosphate capable of passing through an acidic state during hydrolysis or heating, to a dibasic alkaline earth metal orthophosphate yields, upon heating, a phosphate dentifrice polishing composition having improved compatibility toward fluoride and tin (II) ions when combined therewith in an aqueous medium. As an illustration, an intimate mixture containing about 1% monobasic alkaline earth metal orthophosphate, e.g., monocalcium orthophosphate, monohydrate with the remainder dicalcium orthophosphate, dihydrate may be heated at between about 300° C. and 1100° C. to yield a polishing agent having greater compatibility than heretofore typical of the separately heated compounds or mechanical mixtures thereof. As used hereafter, the term "acidic material" is intended to refer to both the initially acidic compounds and those which pass through an acidic state, as defined more precisely, *infra*.

By analysis, all of the compositions produced by the method of the present invention will be found to comprise a predominant proportion of alkaline earth metal pyrophosphate, e.g., $\text{Ca}_2\text{P}_2\text{O}_7$, $\text{Mg}_2\text{P}_2\text{O}_7$, etc., the usual product of high temperature conversion of a dibasic alkaline earth metal orthophosphate, and a minor amount of one or more other phosphates. The composition of these latter phosphates will obviously depend upon which acidic material is selected for addition to the dibasic alkaline earth metal orthophosphate. Although none of the phosphates except the alkaline earth metal pyrophosphates have yet been isolated and identified precisely in terms of chemical formula or structure, it has been discovered that most, if not all, are more water soluble than the alkaline earth metal pyrophosphate with which they are concurrently produced.

The greatest compatibility, at least the greatest improvement thereof, is usually noted where only a relatively small percentage of the acidic material is added. For example, the heating of dimagnesium orthophosphate, trihydrate with about 1% monomagnesium orthophosphate, dihydrate added yields a product having 75% better fluoride compatibility than magnesium pyrophosphate prepared exclusively from "pure" dimagnesium orthophosphate, trihydrate. On the other hand, if large percentages, for instance about 40% or more of the additive is used, the fluoride compatibility will be found to decrease from its optimum value.

A particularly important feature of the invention is our finding that compatibility improves only if the acidic material is added before heating. Although we do not wish to be bound to any specific theory, an appreciable quantity of the acidic material probably reacts during heating with a stoichiometrically equivalent proportion of dibasic alkaline earth metal orthophosphate. Because of practical limitations, ideal contact between the acidic material and the dibasic alkaline earth metal orthophosphate (on the molecular or ionic level) is impossible, especially where the acidic material is in a particulate form, and therefore not all of the acidic material is thought to react intermolecularly with the dibasic alkaline earth metal orthophosphate. That which does not so react is nevertheless changed chemically by elimination of molecular water, e.g., a monocalcium orthophosphate might

convert to a calcium metaphosphate. Thus characterization of the product is rendered even more complicated by virtue of inclusion therein of some extremely insoluble metaphosphate which, because they represent a very minor proportion of the total mixture, cannot be easily found by ordinary analytical methods such as X-ray powder diffraction patterns. The product may also include amorphous phosphates which cannot be routinely detected by X-ray diffraction patterns. All of these possibilities make it virtually impossible to ascribe percentages to the individual components of the product.

Due to formation by inter- and intramolecular dehydration, the compounds contained in the compositions of this invention are intimately combined, in what may be called an intraparticulate mixture. Single particles may contain two or even more condensed phosphates which cannot be separated by mechanical means. The use herein of the term "intimate mixtures" is therefore intended to describe these pyrogenetically formed mixtures of condensed phosphate and to distinguish the same from simple physical admixtures.

The starting materials of the present invention are well-known chemical compounds which, in most case, are available today in commercial quantities. Both the hydrates and the anhydrous forms of these starting materials, especially the dibasic alkaline earth metal orthophosphates, are suitable (the hydrated forms lose water of crystallization easily at the high temperatures of the invention to yield the anhydrous forms). Further, the so-called "stabilized" calcium orthophosphates (such as described in United States Patent 3,066,056), which are prepared by methods that comprise the in situ addition of poly- or pyrophosphoric acid, are also suitable starting materials. However, all other factors being equal, unstabilized dicalcium orthophosphate will furnish a more compatible polishing composition than the "stabilized" material when said composition is prepared by the method of the present invention.

The dibasic alkaline earth metal orthophosphates of the invention include those of calcium, magnesium, beryllium, strontium, and barium. But, by virtue of their availability and low cost, the calcium and magnesium orthophosphates are especially preferred. The acidic materials are likewise readily available compounds. Those which are initially acidic include monocalcium orthophosphate, monomagnesium orthophosphate, orthophosphoric acid, pyrophosphoric acid, sodium acid pyrophosphate, monosodium orthophosphate, urea phosphate, monoammonium orthophosphate, monopotassium orthophosphate and monolithium orthophosphate. Both acidic alkali and alkaline earth metal primary orthophosphate or mixed salts are included generally. Materials which are suitable by virtue of forming an acidic phosphate residue when heated at the temperatures of our method include organic amine and basic ammonium phosphates such as tetraammonium pyrophosphate, sodium ammonium phosphate, and diammonium phosphate. These compounds presumably undergo decomposition at high temperatures forming a residue which reacts much the same as those additives which are initially acidic. The remaining class of additives consists of hydrolyzable phosphates which tend to leave an acidic residue under the conditions of the present method. These have been found to include the alkali and alkaline earth metal metaphosphates such as those of calcium, sodium, magnesium, and potassium.

The following specific examples are given to further illustrate the invention and no unnecessary limitations should be implied therefrom.

Example 1

A large batch of finely milled dicalcium orthophosphate dihydrate was divided into individual portions weighing 400 grams each. To prepare the test sample, one of these 400 gram portions was placed in a stoppered bottle together with 4 grams of monomagnesium orthophosphate

dihydrate and the bottle was thereafter vigorously agitated to thoroughly mix the phosphates. A control sample of 400 grams of dicalcium orthophosphate dihydrate, obtained from the same batch as that in the foregoing test sample, was also selected for this experiment. Each sample was spread out thinly on a No. 7 evaporating dish which was placed in a muffle heater maintained at a temperature of about 650° C. After heating for four hours in the muffle, during which time the temperature was held steady at 650° C., the samples were removed, cooled to room temperature and milled in a Raymond hammer mill. The samples were then tested for tin (II) compatibility by the procedure outlined infra. The polishing agent prepared from the test sample was found 58.7% compatible, while that prepared from the control sample showed, by the same test, a compatibility of 37.3%.

Example 2

Using the same method as described in Example 1, a test sample was prepared containing a mixture of 4 grams of monoammonium phosphate and 400 grams of dicalcium orthophosphate dihydrate. The mixture was heated together with a control sample of "pure" dicalcium orthophosphate in a muffle heater for four hours at about 650° C. Analysis showed that the polishing agents produced from the test sample and control sample were 57.8% and 43.5% compatible to tin (II), respectively.

In order to evaluate the commercial feasibility of preparing the polishing agents of the invention, pilot runs were conducted in small-scale, industrial-type apparatus. Generally, it was found that the method adapts easily (even when using the rather specialized techniques of fluidization) to commercial manufacture, and allows a high degree of quality control, a characteristic of material significance in such application.

Examples of pilot runs made to explore the commercial aspects of our method will now be presented.

Example 3

Several hundred pounds of a dicalcium orthophosphate feed was first prepared by adding a stoichiometric quantity of lime to a dilute orthophosphoric acid solution and collecting the precipitate. This wet orthophosphate was dried in a standard rotary drier and then mixed with 1% of a similarly prepared batch of monocalcium orthophosphate monohydrate in a ribbon blender. About 220 lbs. of the mixture of orthophosphates were charged to the bed chamber of a 2 ft. diameter fluidization reactor, after which fluidization was commenced by passing gases upward through the material. The bed uniformly expanded to a dense, turbulent fluidized state. A hydrocarbon fuel was burned to supply hot gases to concurrently heat and fluidize the bed; combustion rate was adjusted to maintain the bed at a temperature within the range of 650° to 700° C. After about nine hours of heating, additional mixed calcium orthophosphates were fed (through a screw feeder) to the bed and at the same time a stoichiometrically equivalent quantity of converted material was withdrawn. The feed rate was controlled to give a retention time of approximately nine to twelve hours, thereby averaging about 21 lbs. of feed per hour. Continuous feeding and product withdrawal were accomplished over a period of several weeks without fouling the apparatus. Samples of product taken periodically during this time showed compatibilities ranging from about 12% to 57% higher than for similar polishing agents produced from "pure" dicalcium orthophosphate dihydrate in the same apparatus. The product was also found to be a free-flowing, finely divided material equaling or exceeding normal commercial requirements.

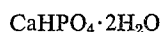
Example 4

A slurry containing 50% solids and weighing 500 lbs. was prepared from a mixture of 99% dicalcium orthophosphate and 1% monocalcium orthophosphate. Using a positive displacement pump the slurry was con-

tinuously fed to the bed chamber of the fluidization unit of Example 3, being sprayed into a pre-established, expanded bed of dry particles having the composition of the product of Example 3. The bed was maintained at about 600° to 700° C. with hot gases emanating from a wind-box-combustion chamber adjacent to the bed at the bottom thereof. Product continuously removed from the bed and sampled was found to be a commercially-acceptable, free-flowing material having a fluoride compatibility higher than for similar polishing agents produced from "pure" dicalcium orthophosphate dihydrate in the same apparatus.

under identical conditions (static heating in ovens at 500° to 900° C.) for the same period of time.

The data of Table I are given especially for the purpose of showing two effects, namely that (1) small percentages of the acidic material will cause an appreciable improvement in compatibility and (2) a wide range of acidic materials may be used. Differences between the compatibilities of the various control samples prepared from



are attributable mainly to the duration of heating.

TABLE I

Percent	Composition of Feed before Heating		Tin (II) Compatibility of Heated (converted) feed, percent
100.0.....	Dicalcium orthophosphate, dihydrate.....	(Control sample).....	33.2
99.0.....	Dicalcium orthophosphate dihydrate.....	(Test sample).....	44.2
1.0.....	Monocalcium orthophosphate, monohydrate.....	(Control sample).....	32.3
100.0.....	Dicalcium orthophosphate, dihydrate.....	(Control sample).....	32.3
99.0.....	Dicalcium orthophosphate, dihydrate.....	(Test sample).....	44.8
1.0.....	Calcium metaphosphate.....	(Control sample).....	37.3
100.0.....	Dicalcium orthophosphate, dihydrate.....	(Control sample).....	37.3
99.0.....	Dicalcium orthophosphate, dihydrate.....	(Test sample).....	58.7
1.0.....	Monomagnesium orthophosphate, dihydrate.....	(Control sample).....	43.5
100.0.....	Dicalcium orthophosphate dihydrate.....	(Control sample).....	43.5
99.0.....	Dicalcium orthophosphate, dihydrate.....	(Test sample).....	57.8
1.0.....	Monoammonium phosphate.....	(Control sample).....	40.2
100.0.....	Dicalcium orthophosphate, dihydrate.....	(Control sample).....	40.2
99.0.....	Dicalcium orthophosphate, dihydrate.....	(Test sample).....	75.5
1.0.....	Monosodium orthophosphate.....	(Control sample).....	45.5
100.0.....	Dicalcium orthophosphate, dihydrate.....	(Control sample).....	45.5
99.0.....	Dicalcium orthophosphate, dihydrate.....	(Test sample).....	61.9
1.0.....	Orthophosphoric acid.....	(Control sample).....	41.3
100.0.....	Dicalcium orthophosphate, dihydrate.....	(Control sample).....	41.3
99.0.....	Dicalcium orthophosphate, dihydrate.....	(Test sample).....	58.2
1.0.....	Urea phosphate.....	(Control sample).....	15.6
100.0.....	Dimagnesium orthophosphate, trihydrate.....	(Control sample).....	15.6
99.0.....	Dimagnesium orthophosphate, trihydrate.....	(Test sample).....	27.2
1.0.....	Monomagnesium orthophosphate, dihydrate.....	(Control sample).....	27.2

Example 5

In order to determine the effects of storage upon mixed phosphate polishing agents the following test was accomplished. By the method described in Example 1, a feed mixture containing 50% $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, 40%



and 10% $\text{MgH}_4(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ was prepared and calcined. It should be noted that this mixture contained only 10% acidic material within the definitions of this specification. After calcination, a portion of the mixed polishing agent was tested and found to have a tin (II) compatibility of 61.9%. The remaining portion was placed in storage at room temperature. After sixty days of storage the sample was found to have a tin (II) compatibility of 51.9%, although at this time the fluoride ion concentration was found to be 74% of theory.

The procedure followed for determining both tin (II) and fluoride compatibilities involves placing a measured quantity of phosphate polishing agent in a flask, adding thereto some distilled water containing a measured quantity of stannous fluoride, and agitating the resulting slurry vigorously. After agitation the slurry is centrifuged and the supernatant liquor is tested for soluble tin (II) and fluoride by well-known analytical methods. The percentage compatibility is measured as the ratio of the unreacted fluoride or tin (II) to the amount originally present.

A comparison between the tin (II) compatibilities of the compositions of the invention and the "pure" compounds of the prior art is shown in Table I wherein the composition of the feed before heating is reported on the left of the table opposite the analytical value for compatibility of the product resulting from heating (converting) said feed. For each feed mixture (the test sample) there is included a control sample consisting entirely of dibasic alkaline earth metal orthophosphate. Also, each couple (i.e., test sample+control sample) was heated

The effect of higher percentages of the acidic additive on compatibility is illustrated in the following table.

TABLE II

[(a) Calcium phosphate compositions prepared from monocalcium orthophosphate-dicalcium orthophosphate mixtures]

Percentage feed as $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (percent by weight):	Tin (II) compatibility (percent)
0.0 (control sample)	32.3
0.5	49.0
1.0	51.6
5.0	58.2
10.0	73.2
50.0	79.1

[(b) Magnesium phosphate compositions prepared from monomagnesium orthophosphate-dimagnesium orthophosphate mixtures]

Percentage feed as $\text{MgH}_4(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (percent by weight):	Tin (II) compatibility (percent)
0.0 (control sample)	15.6
1.0	27.2
7.0	57.6
13.0	55.6
35.0	67.0
50.0	32.0

It is important to note that while the compatibility of the calcium pyrophosphate composition continues to increase at higher percentages of the additive, although at a decreasing rate above about 10%, the magnesium composition reaches a peak compatibility and subsequently declines. This phenomenon is thought to be due to the formation of large quantities of magnesium metaphosphate, a compound having a tin (II) compatibility of only 1.6% in its "pure" form.

The foregoing data indicate that the maximum rate of improvement in compatibility is attained at small percentages of added acidic material, and significant improvement is seldom noted when the acidic material is added in excess of 40% by weight of the feed. Because of the detrimental effect of the additive on various characteristics of the resulting dentifrice polishing agent (e.g., abrasiveness), it is preferable to limit the acidic material to not more than 10% by weight of the feed. As for smaller percentages of acidic material, addition of only 0.33% of monocalcium orthophosphate monohydrate, for instance, has been found to increase compatibility in calcium pyrophosphate from 32.3% to 37.7%, while 0.67% of the additive gives a product having 41.5% compatibility. Polishing agents produced from feed having less than 0.33% additive have not been found to give improved fluoride compatibility. It is nevertheless preferable to use at least 1% acidic material in order to obtain uniform quality and a homogenous product.

At the preferred proportions of acidic material and dibasic alkaline earth metal orthophosphate, the resulting phosphate polishing agent appears to consist of at least 80% to not more than about 99.5% alkaline earth metal pyrophosphate, with the remainder in the form of other condensed phosphates.

It is highly preferable that the mixed feed be thoroughly commingled to obtain maximum contact between the reactants. In order to improve contact between particulate materials, it is desirable that such materials be in a finely divided state, e.g., about 90–100% passing through a 200 mesh screen. However, to some degree, improved polishing agents can be produced even from a relatively coarse feed.

Another feature which should be especially noted is that the acidic material need not have the same cation as the dibasic alkaline earth metal orthophosphate. By the use of feed having various cations, mixed phosphate salts such as sodium calcium polyphosphates and barium magnesium polyphosphates are formed in some appreciable proportions.

The acidic additives of the invention have also been found helpful for ameliorating random variations of fluoride and/or tin (II) compatibilities. Heretofore, commercial preparation often yielded phosphate polishing agents, especially calcium pyrophosphate, having widely different compatibilities between successive product lots, even when preparation was accomplished under well-controlled conditions. Ostensibly, the variations were caused, at least in some cases, by irregularities in the dibasic alkaline earth metal orthophosphates feed. The improved uniformity possible with the additives of the invention is illustrated in Table III, infra. In the table it may be observed that the products formed from feed containing the acidic additive showed far greater uniformity of compatibilities than products prepared from control samples made up from the same lots of dicalcium orthophosphate, dihydrate (but not containing the additive). All of the feed samples shown in the table were statically heated at 650° C. for four hours to accomplish conversion.

The desired calcination temperatures of this invention are essentially the same as heretofore normally used for conversion of dibasic alkaline earth metal orthophosphates to the pyrophosphates. As disclosed in U.S. Patent No. 2,876,166 greater compatibility is achieved if the phosphate feed is heated until complete conversion to the condensed phosphates, although it is preferable to stay below the fusion temperature. The required heating for complete conversion is a rather complex function of the type of heating procedure, temperature and time, and as such is beyond the scope of this invention. In general, however, temperatures between 300° C. and 1100° C. are satisfactory, while a preferred temperature range for either calcium or magnesium phosphate mixtures is 500° C. to 700° C. The duration of heating, while dependent upon the temperature used, may be from about one to sixteen hours, preferably about three to twelve hours for either calcium or magnesium phosphates.

The improved compositions of this invention may be used in toothpastes, toothpowders or any aqueous media containing a soluble fluoride suitable for oral application to the teeth. The fluorides with which such compositions are compatible include SnF₂, NaF, ZnF₂, SnF₄, CrF₃, LiF, KF, CuF₂, and NH₄F, while among these the SnF₂ and NaF are considered especially suitable.

A typical toothpaste containing our more compatible polishing compositions may have the following ingredients: from 30% to 50%, usually about 40%, of the compositions of the invention; from 0.04% to 1.6%, preferably about 0.4% of a soluble fluoride such as stannous fluoride; from 15% to 30% of a humectant such as glycerine and/or sorbitol to suspend the solids; about 1% to 2% of a binder (or gum) such as an Irish moss or carboxymethyl cellulose; about 1% to 2% of a synthetic detergent; from 1% to 2% of a preservative for the gum (prevents mold, etc.) such as ethyl paracet; a minor amount up to about 1% of a flavoring agent; and sufficient water, usually from 15% to 25%, to expand the gum and thin the paste to a suitable consistency.

As shown hereinbefore, the acidic additives of the invention will normally comprise less than 50% by weight of the total feed material. In most applications, however, fluoride compatibility will be significantly improved by very minor amounts of the additive, in most cases below 10% by weight. The usual method of addition of the additive material is by physical admixture with a dry dibasic alkaline earth metal orthophosphate, but as shown above in Example 4, variations such as liquid feed are possible. Another practical method of applying the additive comprises forming a solution or slurry of the additive and spraying said solution or slurry upon either a static or agitated bed of the dibasic alkaline earth metal orthophosphate. Other methods of applying the additive will be apparent from the nature of the above disclosure.

The foregoing detailed description has been given for clearness of understanding only, and no unnecessary limitations should be understood therefrom, as modifications will be obvious to those skilled in the art.

TABLE III

Percent	Composition of Feed before Heating		Tin (II) Compat- ibility, Percent	Fluoride Compat- ibility, Percent
100.0	Dicalcium orthophosphate, dihydrate	(Control sample)	38	32
99.0	Dicalcium orthophosphate, dihydrate	(Test sample)	51	38
1.0	Monocalcium orthophosphate, monohydrate	(Control sample)	31	24
100.0	Dicalcium orthophosphate, dihydrate	(Control sample)	31	24
99.0	Dicalcium orthophosphate, dihydrate	(Test sample)	51	46
1.0	Monocalcium orthophosphate, monohydrate	(Control sample)	37	20
100.0	Dicalcium orthophosphate, dihydrate	(Control sample)	37	20
99.0	Dicalcium orthophosphate, dihydrate	(Test sample)	50	44
1.0	Monocalcium orthophosphate, monohydrate	(Test sample)	50	44

We claim:

1. Method of manufacturing a dentifrice polishing agent consisting of an intraparticulate mixture of condensed phosphates which comprises heating at a temperature within the range from 300° C. to 1100° C., 90% and 99.67% of a dibasic alkaline earth metal orthophosphate having thoroughly commingled therewith between 0.33% and 10% of at least one compound selected from the group consisting of inorganic acidic phosphates, hydrolyzable alkali and alkaline earth metal metaphosphates, and phosphates which transitionally yield inorganic acidic phosphates residue when heated at a temperature within the range from 300° C. to 1100° C., for a time sufficient to accomplish substantially complete conversion to the condensed phosphates.

2. Method of manufacturing a dentifrice polishing agent consisting of an intraparticulate mixture of condensed phosphates which comprises heating, at a temperature within the range from 300° C. to 1100° C., between 90% and 99.67% of a dibasic alkaline earth metal orthophosphate having thoroughly commingled therewith between 0.33% and 10% of at least one compound selected from the group consisting of monocalcium orthophosphate, calcium metaphosphate, monomagnesium orthophosphate, monoammonium orthophosphate, monosodium orthophosphate, orthophosphoric acid, pyrophosphoric acid, urea phosphate, tetraammonium pyrophosphate, sodium acid pyrophosphate, monopotassium orthophosphate, monolithium orthophosphate, sodium ammonium phosphate, diammonium phosphate, sodium metaphosphate, magnesium metaphosphate, and potassium metaphosphate, for a time sufficient to accomplish substantially complete conversion to the condensed phosphates.

3. Method of manufacturing an intraparticulate mixture of condensed calcium phosphates which comprises heating for 3 to 12 hours, at a temperature within the range of from 500° C. to 700° C., a finely divided dicalcium orthophosphate having thoroughly commingled therewith at least 0.33 but not more than 10% finely divided monocalcium orthophosphate.

4. Method of manufacturing an intraparticulate mixture of condensed magnesium phosphates which comprises heating for 3 to 12 hours, at a temperature within the range of from 500° C. to 700° C., a finely divided dimagnesium orthophosphate having thoroughly com-

mingled therewith at least 0.33 but not more than 10% finely divided monomagnesium orthophosphate.

5. An intraparticulate mixture of condensed calcium phosphates resulting from substantially complete molecular dehydration of a finely divided feed comprising a physical admixture of between 90% and 99.67% dicalcium orthophosphate and between 0.33% and 10% monocalcium orthophosphate.

6. An intraparticulate mixture of condensed magnesium phosphates resulting from substantially complete molecular dehydration of a finely divided feed comprising a physical admixture of between 90% and 99.67% dimagnesium orthophosphate and between 0.33% and 10% monomagnesium orthophosphate.

7. As a dentifrice polishing agent an intraparticulate mixture of condensed phosphates resulting from substantially complete molecular dehydration of a finely divided feed consisting of a physical admixture of between 90% and 99.67% of a dibasic alkaline earth metal orthophosphate and between 0.33% and 10% of at least one compound selected from the group consisting of monocalcium orthophosphate, calcium metaphosphate, monomagnesium orthophosphate, monoammonium orthophosphate, monosodium orthophosphate, orthophosphoric acid, pyrophosphoric acid, urea phosphate, tetraammonium pyrophosphate, sodium acid pyrophosphate, monopotassium orthophosphate, monolithium orthophosphate, sodium ammonium phosphate, sodium metaphosphate, magnesium metaphosphate and potassium metaphosphate.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,269,814

August 30, 1966

Lowell E. Netherton et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 44, for "MgHPO $\cdot$ 3H $_2$ O" read -- MgHPO $_4$ $\cdot$ 3H $_2$ O --;
column 9, line 12, strike out "residue".

Signed and sealed this 1st day of August 1967.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents