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## DENTIFRICE PREPARATIONS

William H. Nebergall, Bloomington, Ind., assignor to Indiana University Foundation, Bloomington, Ind., a corporation of Indiana

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This invention relates to dentifrice compositions, particularly toothpastes, which, in spite of the presence of a calcium-containing polishing agent for cleaning the teeth, are capable of furnishing fluorides to the teeth for their known prophylactic function of protecting the teeth against caries.

It has been known for some time that the presence of fluorides in very small amounts in the drinking water reduces the incidence of caries in the population using such water. Even limited topical applications to the teeth of somewhat more concentrated aqueous solutions of fluoride, when made under proper conditions, have met with dramatic success in the prevention of tooth decay in children, and this practice is a preventative measure which is generally recognized and widely used by the dental profession today.

Efforts have also been made to provide fluorides to the teeth through the medium of a conventional dentifrice designed for regular self-use in the customary manner of practicing personal oral hygiene in the home in conjunction with a tooth brush, but such efforts have always been severely handicapped by the tendency for the fluoride to be inactivated and rendered unavailable by the other ingredients of a dentifrice especially the calcium-containing polishing agents.

It is an object of this invention to provide dentifrices suitable for home use which, when brushed on the teeth, not only perform the cosmetic functions of cleaning and polishing the teeth but also effectively furnish fluorides in solution, readily available to the teeth for the prophylactic functions of protecting the teeth against decay and diminishing the incidence and limiting the severity of carious lesions therein.

A further object of my invention is the provision of calcium-containing dental polishing agents which are more compatible with fluorides and can be incorporated in dentifrice preparations containing fluoride with a minimum loss of fluoride to the inactive water-insoluble form.

It is also an object of this invention to provide a method of treating conventional calcium-containing polishing agents in order to render them more compatible with the fluorides with which they are combined in a given dentifrice.

Other objects and features of this invention will be apparent from the detailed description and explanation of the invention which follows.

I have discovered that the inactivation of fluorides in dentifrices is most often due to the presence of an incompatible polishing agent. Calcium orthophosphates, especially dicalcium orthophosphate, are among the most popular of dentifrice polishing agents for conventional use but have not proved suitable for use with fluorides. I have discovered, however, that these calcium orthophosphates may be made more compatible with fluorides if they are heat-treated in a certain manner prior to incorporation into the dentifrice mix.

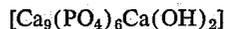
Thus, it has been found that more of the fluorine contained in the dentifrice mix is retained in the water-soluble

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anti-caries active form if heat-treated calcium orthophosphates or calcium salts of molecularly dehydrated phosphoric acids such as calcium pyrophosphates, calcium metaphosphates and calcium polyphosphates, are used in place of the ordinary calcium orthophosphates. In general, it is necessary to carry out the heat treatment of the calcium orthophosphates at temperatures above 200° C. and temperatures considerably above 250° C. are usually preferred because the duration of treatment required to accomplish a given improvement in fluoride compatibility of a given orthophosphate is less at the higher temperatures. The temperature should not be so high as to cause incipient fusion of the phosphate, however, since additional steps would then be required to reduce the mass to a finely divided powder of dentifrice grade.

The exact chemical or physical mechanism by which the calcium orthophosphates are made more compatible by means of heat-treatment is only partially understood, but it is known that extensive changes in these polishing agents do occur during the course of this heat treatment. In the case of dicalcium orthophosphate and monocalcium orthophosphates molecular dehydration definitely takes place and these materials are converted ultimately by sufficient heat treatment into calcium pyrophosphates, and calcium metaphosphates respectively. The changes which take place in the case of heat treating precipitated tricalcium orthophosphates also involve the loss of tightly held water from some source, the exact nature or character of which has not been definitely ascertained.

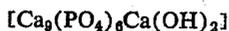
It appears that the application of the name tricalcium orthophosphate and the formula,  $\text{Ca}_3(\text{PO}_4)_2$ , to precipitated orthophosphates is wholly inaccurate in most cases and actually is misleading even when the analysis of the precipitate empirically conforms to said formula. Although such products sold commercially are generally referred to in this manner or as tri-basic calcium orthophosphates and the National Formulary even describes precipitated calcium phosphate as  $\text{Ca}_3(\text{PO}_4)_2$ , it is generally recognized that the chemical and X-ray analysis of such products generally corresponds more closely to the compound known as hydroxylapatite



Thus, the Ca/P ratio of such products is generally nearer to the figure of 1.67, which is theoretical for the above formula for hydroxylapatite than to 1.5, which is theoretical for  $\text{Ca}_3(\text{PO}_4)_2$ . However, such precipitated products are not absolutely consistent either as to chemical analyses or X-ray patterns and there is not even complete agreement among the phosphate experts as to the unique character of any given hydroxylapatite species. In fact, precipitated products all showing the hydroxylapatite X-ray pattern but having Ca/P ratios varying not only between 1.5 and 1.67 but considerably above 1.67 have been reported. See the review on tribasic calcium phosphates by Eisenberger, Lehrman and Turner in Chemical Reviews 26, 257-96 (1940). Such variations in composition have also been discussed by many others, such as Hodge, Lefevre and Bale who suggest in an article in the Analytical Edition of Industrial and Engineering Chemistry 10, 156-161 (1938) that the particular empirical composition obtained may be determined by the mode of precipitation and that Ca/P ratios above 1.67 may be obtained when precipitation occurs in the presence of an excess of calcium while Ca/P ratios below 1.67 may result from the presence of an excess of phosphate. The soundest assumption seems to be that these precipitates, in most cases, do not represent any single particular chemical specie but a solid solution the composition of which is continuously variable over a considerable range of mixtures more alkaline than dicalcium orthophosphate ( $\text{CaHPO}_4$ ).

The discussion of the preceding paragraph not only describes the possible variations in composition of products included within the scope of the terms "precipitated tricalcium orthophosphates" but also helps to account for the presence in such products of the rather tightly held water referred to previously. The amount of this water, like the composition of the precipitate, is variable but averages around 6 to 8%. This water has frequently been referred to as water of hydration. Thus, the complete formula for the precipitated orthophosphate has been described as  $\text{Ca}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ . However, the inaccuracy of describing this water as true water of hydration is generally as well recognized as is the inaccuracy of the  $\text{Ca}_3(\text{PO}_4)_2$  structure itself, because (1) the amount of this water is not a constant percentage of the weight even for a given Ca/P ratio and (2) this water is more difficult to remove than the customary water of hydration requiring temperatures of from 200 to 800° C. for removal. The most satisfactory explanation seems to be that this water content is present in one or more of three forms, namely (1) as OH groups in the hydroxylapatite lattice, (2) in  $\text{Ca}(\text{OH})_2$  or  $\text{H}_3\text{PO}_4$  adsorbed or occluded within the particles of "precipitated tricalcium orthophosphate" or (3) as molecular water adsorbed or occluded within the particles of "precipitated tricalcium orthophosphate." Evidences and suggestions of the presence of these forms have been presented by several workers including Hodge, Lefevre and Bale (see above), Hendricks and Hill in Proceedings of the National Academy of Sciences 36, 731-737 (1950), and Posner and Stephenson in Journal of Dental Research 31, 371-382 (1952).

It is evident, therefore, that so called precipitated tricalcium orthophosphates contain a considerable amount of water which is present neither as free moisture nor as true water of hydration and most of which requires temperature well above 200° C. for removal. This is the water in "precipitated tricalcium orthophosphates" which, whether it is adsorbed, occluded or combined, is referred to as water more tightly held than true water of hydration. Loss of this water and/or changes in crystal size are the only significant changes noted on heat treating "precipitated tricalcium orthophosphates" below 700-800° C. However, if the initial empirical composition of the precipitated orthophosphate is fairly close to the formula  $\text{Ca}_3(\text{PO}_4)_2$ , the material tends to be converted by sufficient heat treatment to  $\beta$ -tricalcium phosphate and ultimately to  $\alpha$ -tricalcium phosphate, entirely different crystalline forms which can be distinguished by means of X-rays from the initial precipitate having the typical hydroxylapatite X-ray pattern. If the initial empirical composition of the precipitated orthophosphate is fairly close to the hydroxylapatite formula



the material tends to be converted by sufficient heat treatment to oxyapatite  $[\text{Ca}_{10}(\text{PO}_4)_6\text{O}]$  which is also distinguishable by X-rays. Bale et al. in the Analytical Edition of Industrial and Engineering Chemistry 17, 491-495 (1945) and MacIntire, Palmer and Marshall in Industrial and Engineering Chemistry 31, 164-169 (1945), give X-ray diffraction pattern data for these various forms of treated and untreated calcium orthophosphates.

It is possible, of course, depending upon the exact composition of the initial precipitate and the particular heat treating cycle used, to obtain a mixture of one or more of the several different high temperature forms referred to above. In any case, in the presence of water and especially at reduced temperatures, all of these high temperature forms tend to revert gradually after heat treatment to structures which show the hydroxylapatite X-ray pattern and, therefore, most of the heat-treated calcium orthophosphates when actually used in a dentifrice prepa-

ration will show predominantly the hydroxylapatite pattern.

At the present time fluoride-compatible abrasives for use in the present invention are most readily obtained by heat treating conventional calcium orthophosphate abrasives since these latter materials are readily available in the proper form for use in dentifrices. I have found that the maximum increase in fluoride compatibility is obtained by heat treating said calcium orthophosphates to the point of complete conversion to the end products discussed above, namely  $\beta$ - or  $\alpha$ -tricalcium orthophosphate or calcium oxyapatite, calcium pyrophosphates and calcium metaphosphates but for the sake of avoiding additional steps of regrinding and classifying to proper particle size it is preferred that fusion be avoided during heat treatment. In heat treating monocalcium orthophosphates or mixtures containing same, the preferred temperatures are above 200° C. but should not exceed 900° C.; with dicalcium orthophosphates alone, temperatures from 300 to 1100° C. are most usable; while with precipitated tricalcium orthophosphates beneficial heat treatment may be effected at any temperature from 300 to 1500° C. although almost never is there an additional advantage to be gained in heating the material above 1300-1400° C. and generally temperatures above 1000 to 1100° C. would not be preferred. It should be remembered that when mixtures of the above species or when mixed salts containing other metal cations in addition to calcium are treated, the fusion temperatures will tend to be lowered and restriction of temperatures to the upper limits given above can not be strictly relied upon to avoid incipient fusion.

It should also be pointed out that the above described end products themselves, i. e.  $\beta$ - and  $\alpha$ -tricalcium orthophosphates, calcium oxyapatites, calcium pyrophosphates, and calcium metaphosphates or any distinctly characterized intermediate products such as calcium triphosphate ( $\text{Ca}_5\text{P}_6\text{O}_{20}$ ) or other polyphosphates or mixtures of any of these, regardless of whether they have been prepared by heat-treatment directly from the corresponding conventional calcium orthophosphates, or by precipitation from other salts or from the molecularly dehydrated acids, or otherwise, may be used, in the appropriate range of particle sizes, as the fluoride-compatible abrasives of the present invention. As used in the claims the term "calcium metaphosphate" refers to a monomeric compound represented by the formula  $\text{Ca}(\text{PO}_3)_2$ , and the term "calcium polyphosphates" refers to polymeric calcium phosphates, whether in the form of rings or straight chains, and includes calcium pyrophosphate (calcium dipolyphosphate). Although straight calcium salts are preferred, mixed salts containing both calcium and other metal cations in addition are also included within the scope of this invention.

The following specific examples illustrate some procedures which can be followed in preparing my fluoride-compatible polishing agents.

#### Example I

A suitable amount of powdered dentifrice grade dicalcium orthophosphate dihydrate is spread out in a uniform layer on a clean ceramic receptacle and placed in a muffle furnace or other indirect heat-source at a temperature of 815° C. After about 1 hour at this temperature the sample is removed and is found to be almost entirely converted to calcium pyrophosphate ( $\text{Ca}_2\text{P}_2\text{O}_7$ ). The improved compatibility of this material towards fluoride is illustrated by the following experiments:

0.85 g. samples of the abrasive before and after heat treatment were shaken for a period of 5 hours with 25 ml. portions of a solution containing 1000 p. p. m. of fluorine (added as  $\text{SnF}_2$ ), and then the mixtures were set aside for 18 hours for sedimentation of the solid phase. The liquid phase from each sample was then

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centrifuged and aliquots of the appropriate size to contain no more than 50 micrograms of original fluorine were taken of the clear supernatant liquid after centrifugation. The samples were analyzed for fluorine by means of the well known Willard and Winter procedure which includes distillation in the presence of perchloric acid and titration of the distillates against thorium nitrate in the presence of alizarin sulfonate. Hydroxylamine hydrochloride and sodium chloride were added to the distillates before the titrations in accordance with the recommendation of H. A. Williams in the Analyst 71, 175 (1946).

In this manner it was found that 59% of the fluoride originally present was still in solution in the sample shaken with the heat-treated abrasive while only 5.6% of the original fluoride was left in the solution shaken with the untreated abrasive.

Instead of heating at a temperature of 815° C. for one (1) hour as in the above example, substantially the same beneficial results can be secured by heating for 6 hours at 400° C.

Substantially the same results can be obtained if either calcium triphosphate or a mixed salt such as calcium sodium pyrophosphate ( $\text{CaNa}_2\text{P}_2\text{O}_7$ ) is substituted for the heat-treated abrasive in the preceding test.

Dentifrice grade dicalcium orthophosphate dihydrate usually contains a fraction of a percent of a stabilizer, such as  $\text{Na}_4\text{P}_2\text{O}_7$  or  $\text{Mg}_3(\text{PO}_4)_2$ , added for the purpose of preventing loss of water of hydration during long-time storage at climatic temperatures. However, in the above example it is immaterial whether these stabilizers are present, and dicalcium orthophosphate dihydrate containing either, both, or neither of these stabilizers, or even anhydrous dicalcium orthophosphate could be substituted as starting materials in the above experiments without nullifying the beneficial effects of the heat treatment. Anhydrous dicalcium orthophosphate is not appreciably more compatible with fluoride ion than is the corresponding dihydrate, and heat treatment which is sufficient only to remove water of hydration is of very little benefit.

#### Example II

A quantity of powdered monocalcium orthophosphate monohydrate spread in a uniform layer on a clean, unreactive heat-resistant surface is placed in an oven heated to a uniform and constant temperature of 650° C. After 2 hours at this temperature the treated material is found to be almost completely converted to calcium metaphosphate and much more compatible with fluorides than formerly as shown by the following experiment.

The fluoride compatibility of this heat-treated phosphate was compared with that of the untreated monocalcium orthophosphate monohydrate by the same procedure used in Example I. In this way it was found that all of the original fluoride remained in the solution which had been in contact with the heat-treated phosphate while only about 5% of the original fluoride was left in the solution which had contacted the untreated abrasive.

#### Example III

Precipitated dentifrice grade tricalcium orthophosphate meeting specifications set out by the National Formulary is subjected to a temperature of 815° C. for 1 hour. The treated material is found to be greatly improved over the original tricalcium phosphate with respect to fluoride-compatibility as shown by the figures obtained on available fluoride remaining in a solution originally 1000 p. p. m. in fluorine (as  $\text{SnF}_2$ ) after contacting samples of same with measured quantities of the respective abrasives. These figures were 50% available from the heat treated material but only 12% from the control. Such moderate heat treatment does not produce a preferred abrasive of this invention.

If the heat treatment of the original precipitated den-

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tifrice grade tricalcium orthophosphate is continued for 2 hours or more at any temperature above about 900° C., the loss of water is almost completed and the tricalcium orthophosphate is converted almost entirely to the  $\beta$ -form or to calcium oxyapatite or mixtures of the two. Continued heating to temperatures above 1115° C. will generally result in appreciable conversion of any  $\beta$ -tricalcium phosphate to the  $\alpha$ -form, sometimes called  $\gamma$ -phase. These phase changes are discussed in the review by Eisenberger, Lehrman and Turner mentioned before.

The above examples, which describe the simplest form of dentifrice composition contemplated by the present invention, i. e. the simple mixture of abrasive and fluoride, demonstrate most directly and clearly the improvement in fluoride-compatibility of the specially heat-treated calcium orthophosphates or molecularly dehydrated calcium orthophosphates over the conventional calcium orthophosphate dentifrice abrasives. The additional examples which follow illustrate in more detail some of the finished dentifrice compositions which can be prepared by the use of abrasives of the class which I have discovered to be more compatible with fluorides than are the conventional dentifrice abrasives, which class includes such well-characterized chemical species as calcium pyrophosphates, calcium polyphosphates, calcium metaphosphates,  $\beta$ - and  $\alpha$ -tricalcium orthophosphates and calcium oxyapatite. These additional examples will also serve to indicate some of the preferred conditions for the preparation and use of such dentifrice preparations.

#### Example IV

Some of the calcium pyrophosphate prepared in Example I by heating dicalcium orthophosphate dihydrate for one hour at a temperature of 815° C. was used in making a fluoride-containing toothpaste of the following composition:

	Parts by weight
Heat-treated $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ -----	41.6
Synthetic detergent -----	1.4
Glycerine -----	25.0
Water -----	28.0
Irish moss extract -----	1.5
Stannous fluoride -----	1.6
Flavorings -----	0.9
Total -----	100.0

The procedure for preparing the toothpaste of the above composition was as follows:

The Irish moss extract was wet out in part of the glycerine and the calcium pyrophosphate was wet out in part of the water, in which the synthetic detergent had been dissolved. These slurries were then mixed together with heating until a uniform temperature of 70° C. was reached. The thickened paste mixture was then cooled to a temperature of 35° C. and the flavoring, the remaining glycerine and the remaining water containing the stannous fluoride were all added and mixed in thoroughly to give a homogeneous paste of suitable consistency.

This paste was then compared for its ability to release fluoride in solution with a similar product of the same composition with the one exception that untreated dicalcium orthophosphate was used as the abrasive instead of the heat-treated material which had been converted largely to pyrophosphate by the heat-treatment. The comparison test was made by analyses of the supernatant liquid phases obtained from slurries of the pastes in water.

The analytical technique was as follows:

Slurries were made by shaking 15 g. of the dentifrice with 45 g. of water in 100 ml. screw cap glass bottles for 30 minutes. The liquid phase was withdrawn after most of the solid matter had settled out and was centrifuged at 15,000 R. P. M. for 1 hour in order to separate

out the remaining solids. Aliquots of the appropriate size to contain no more than 50 micrograms of fluoride were taken of the clear supernatant liquid phases and added to 1 g. of samples of calcium oxide. These mixtures were then evaporated to dryness and ignited to remove organic matter. Then the available fluoride content was determined by the Williams' modification of the Willard and Winter perchloric acid distillation and thorium nitrate titration, just as for the tests on the abrasives alone, as described in Example I above.

In this manner it was determined that about 16% of the total fluoride content originally added to the paste was available in water-soluble anti-caries active form in the paste made from the heat-treated abrasive while only about 8% of the total fluoride was available in the control paste. In a similar paste made with anhydrous dicalcium orthophosphate only 6% of the original fluoride was found in the supernatant liquid obtained from its slurry.

The greater effectiveness of the fluoride dentifrices prepared with my heat-treated abrasives in protecting the teeth against attack by acids and the carious process has also been demonstrated by extensive acid solubility studies on tooth enamel (both whole and powdered) before and after treatment with slurries of the test dentifrices described in this and the following examples.

The improved effectiveness of fluorine-containing compounds which normally dissociate to yield fluoride ions (F<sup>-</sup>) in aqueous solution when used in dentifrices containing calcium pyrophosphate or any other heat-treated calcium orthophosphate in place of conventional calcium orthophosphates can be readily noted with pastes containing any concentration of fluoride-producing fluorine from 100 p. p. m. on up instead of the 1.6% stannous fluoride used above, which is equivalent to 4000 p. p. m. F. However, a limit of 4000 p. p. m. of fluorine is tentatively made for reasons of safety in avoiding any possibility of fluorine toxicity from the regular use of such dentifrices. This safety limit is figured on the improbable assumption that all of the fluoride in the average amount of paste used by a human-being over any given period of time would actually be ingested. Thus, this limit is obviously very conservative. All things considered, the preferred concentration is about 0.1% fluoride-producing fluorine (or about 0.4% stannous fluoride) which is equivalent to about 1000 p. p. m. F. In any case it is believed that there would seldom be any significant additional advantage in using more than 1% fluoride-producing fluorine (≈10,000 p. p. m.) in the composition of the present invention regardless of toxicity questions, which have not yet been fully settled for products of this type. These fluorine concentrations may be furnished in the form of any non-toxic fluorine-containing compounds, which normally dissociate in aqueous solution to yield fluoride ions including fluorides such as NaF, SnF<sub>2</sub>, ZnF<sub>2</sub>, SnF<sub>4</sub>, CuF<sub>2</sub>, NH<sub>4</sub>F, KF, LiF, CrF<sub>2</sub>, the more complex fluorine-containing salts of the same metals or ammonia such as the fluosilicates e. g. Na<sub>2</sub>SiF<sub>6</sub>, and also fluotitanates etc., as well as mixed halides such as chlorofluorides of the same metals or ammonia, e. g. SnClF.

Substitutions can be made freely with respect to all the remaining ingredients of these pastes without affecting the beneficial results obtained by the practice of this invention. Thus sorbitols, glycols, or silicones may be used in place of glycerine and the proportion of water and glycerine or other organic vehicle may be reduced or increased provided consistency is maintained by suitable adjustment in the amounts of the other ingredients.

In general, a toothpaste made according to the teachings of this invention will contain about 0.01 to 0.4% of fluorine (F), 10-40% water, 10-40% glycerine or other polyhydric alcohol, and 20-60% of my fluoride-compatible calcium phosphate compounds. Gum tragacanth and other natural gums, or alginates and other

mucilaginous vegetable extracts of land or sea origin may be used in place of the Irish moss extract. And, of course, wide freedom of choice is possible in selecting the detergents and flavorings to be used. Any other additional ingredients suitable for dentifrice use which are compatible with the particular fluorine compounds employed may also be used. No special problems are introduced by the use of calcium pyrophosphate or my other heat treated calcium orthophosphates since they are even less reactive and therefore more stable and compatible not only with the fluorides but also with almost any other possible dentifrice ingredient than are the more conventional polishing agents such as dicalcium orthophosphate, precipitated tricalcium orthophosphate, etc.

Additional specific examples of dentifrice compositions prepared according to the teachings of this invention are the following.

Example V

A commercial sample of calcium pyrophosphate prepared in proper form (particle size, softness, etc. for dentifrice use was incorporated in a fluoride-containing toothpaste of the following composition:

	Parts by weight
Calcium pyrophosphate-----	42.2
Synthetic detergent-----	1.3
Glycerine -----	25.0
Water -----	29.0
Gum tragacanth-----	1.4
Sodium fluoride-----	0.2
Flavorings -----	0.9
Total -----	100.0

The process of preparing this paste was as follows:

The gum tragacanth was wet out in part of the glycerine; the synthetic detergent and the sodium fluoride were dissolved in the water and the remaining glycerine added to this solution. The pyrophosphate was then wet out in the aqueous mixture and this slurry was then mixed with the gum tragacanth slurry and the combined mass was heated to 65° C. and cooled to 32° C. while being mixed continuously. Finally the flavor was added and mixed in thoroughly to give a homogeneous finished paste product. The superiority of this toothpaste over a similar product containing the same amount of fluoride but with dicalcium orthophosphate dihydrate as the abrasive can be seen from the following results of analyses for available fluoride in slurries of the two products. These analyses were carried out according to the procedure described in Example IV above and showed about 36% of the original fluorine in available form in the pyrophosphate paste compared to only 3% in the control paste.

In order to secure the beneficial effects of the dentifrice compositions of my invention on the teeth it is only necessary to apply these products to the various tooth surfaces by means of a brush much in the usual manner of practicing oral hygiene in the home. In order to obtain the maximum benefits from the use of these products they should be applied in the greatest possible strength as thoroughly as possible to all of the tooth surfaces which can be reached. A paste-form product is preferred since this type of dentifrice is easiest to handle on a brush and apply to the teeth without adding moisture other than that in the mouth and at the same time the available fluoride-content in a paste dentifrice is already dissolved and ready for immediate activity on the tooth surfaces.

Example VI

The heat-treated monocalcium orthophosphate prepared in Example II by heating conventional monocalcium orthophosphate for 2 hours at 650° C. was used in

making a fluoride-containing powder dentifrice according to the following formulation:

	Parts by weight	
Heat-treated monocalcium orthophosphate (from Example II)-----	95.0	5
Synthetic detergent-----	3.3	
Stannous fluoride-----	0.5	
Flavoring-----	1.2	
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Total-----	100.0	10

The available fluoride in a slurry of this dentifrice was determined by the same procedure described in connection with the analyses of Example IV and was found to be 100% of that added as SnF<sub>2</sub>. In contrast, a similar tooth powder prepared with unheat-treated monocalcium orthophosphate yielded only 49% of its total fluoride in available form when analyzed in the same way.

Use of a commercial calcium metaphosphate in the above toothpowder formula considerably increased the amount of available fluoride over that of the control powder containing monocalcium orthophosphate though not to the level of 100% as found in the product made with heat-treated monocalcium orthophosphate.

It is obvious that the above examples are illustrative only of the many possible variations of which my invention is susceptible and in no way exhaustive of the innumerable combinations of fluorine-containing ingredients and heat-treated calcium orthophosphate polishing agents which it is possible to use in gaining the beneficial results of my invention. Accordingly the scope of my invention should not be limited by the above examples but only to the composition ranges specified in the following claims. As used herein the term calcium orthophosphates shall be understood to apply generally to all of the known and recognized species which can be formed by precipitation of mixing Ca<sup>++</sup> ions and PO<sub>4</sub><sup>---</sup> ions in aqueous solution, whether in the presence or absence of other metal cations, including specifically the hydroxylapatite structure and mixed salts containing both calcium and other metal cations.

What I claim as new and desire to protect by United States Letters Patent is:

1. A dentifrice combining a fluorine-containing compound and an abrasive, in which said fluorine-containing compound is one which normally dissociates to yield fluoride ions in aqueous solution, and which is present in said dentifrice in an amount which contains at least 0.01%, by weight, of ionizable fluoride but not more than 0.4%, by weight, total fluorine, and in which said abrasive is present as at least 20%, by weight, of said dentifrice and comprises essentially at least one material selected from the group consisting of calcium polyphosphates, calcium metaphosphate, calcium oxyapatite, and  $\beta$ - and  $\alpha$ -tricalcium orthophosphates.

2. The dentifrice of claim 1 in which the fluorine-containing compound is stannous fluoride and the calcium polyphosphate is calcium pyrophosphate.

3. The dentifrice of claim 1 in which the fluorine-containing compound is sodium fluoride and the calcium polyphosphate is calcium pyrophosphate.

4. The dentifrice of claim 1 in which the fluorine-containing compound is stannous fluoride and the abrasive comprises essentially calcium metaphosphate.

5. The dentifrice of claim 1 in which the fluorine-containing compound is sodium fluoride and the abrasive comprises essentially calcium metaphosphate.

6. The dentifrice of claim 1 in which the fluorine-containing compound is stannous fluoride and the abrasive comprises essentially  $\beta$ -tricalcium orthophosphate.

7. The dentifrice of claim 1 in which the fluorine-containing compound is sodium fluoride and the abrasive comprises essentially  $\beta$ -tricalcium orthophosphate.

8. The dentifrice of claim 1 in which the fluorine-con-

taining compound is sodium fluoride and the abrasive comprises essentially calcium triphosphate.

9. The dentifrice of claim 1 in which the fluorine-containing compound is stannous fluoride and the abrasive comprises essentially calcium triphosphate.

10. The dentifrice of claim 1 in which the fluorine-containing compound is stannous fluoride and the abrasive comprises essentially calcium polyphosphate.

11. The dentifrice according to claim 1 in which the fluorine-containing compound is sodium fluoride and the abrasive comprises essentially calcium polyphosphate.

12. A toothpaste combining a fluorine-containing compound and an abrasive, in which said fluorine-containing compound is one which normally dissociates to yield fluoride ions in aqueous solution and which is present in said dentifrice in an amount which contains at least 0.01%, by weight, of ionizable fluoride but not more than 0.4%, by weight, of total fluorine, and in which said abrasive is present as from 20% to 60%, by weight, of said dentifrice and comprises essentially at least one material selected from the group consisting of calcium polyphosphates, calcium metaphosphate, calcium oxyapatite, and  $\beta$ - and  $\alpha$ -tricalcium orthophosphates.

13. The toothpaste of claim 12 in which the fluorine-containing compound is stannous fluoride.

14. The toothpaste of claim 13 in which the calcium polyphosphate is calcium pyrophosphate.

15. The toothpaste of claim 12 in which the fluorine-containing compound is sodium fluoride.

16. The toothpaste of claim 15 in which the calcium polyphosphate is calcium pyrophosphate.

17. A toothpaste comprising by weight from about 10% to 40% of water, from about 10% to 40% glycerine, stannous fluoride in an amount equivalent to 0.01% to 0.4% of fluorine, and from about 20% to 60% of calcium pyrophosphate.

18. A toothpaste comprising by weight from about 10% to 40% of water, from about 10% to 40% of glycerine, sodium fluoride in an amount equivalent to 0.01% to 0.4% of fluorine and from about 20% to 60% of calcium pyrophosphate.

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