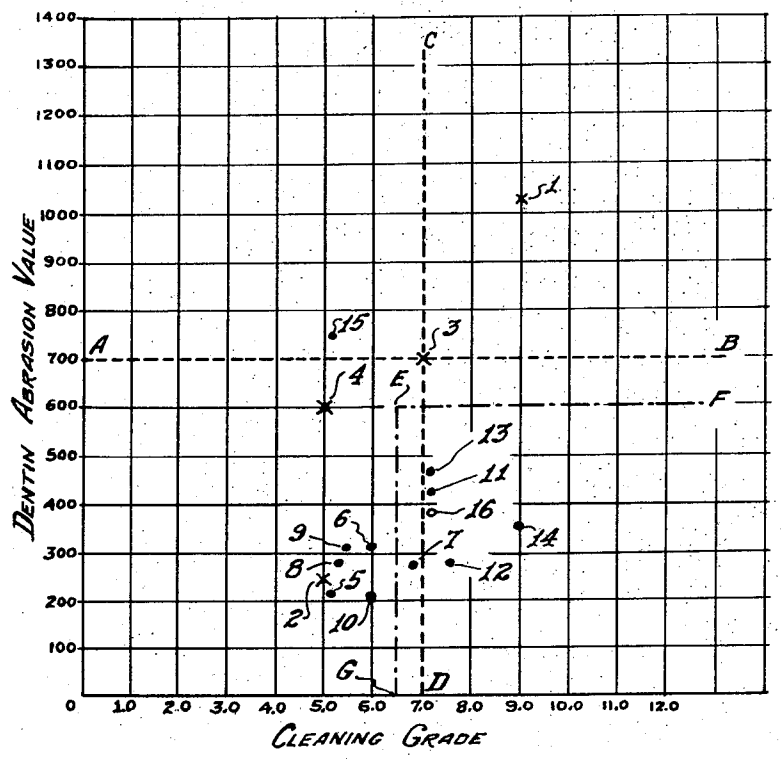
March 3, 1959 R. W. BROGE ET AL 2,876,168

CALCIUM PYROPHOSPHATE ABRASIVE AND DENTIFRICE CONTAINING THE SAME

Filed Aug. 20, 1956 2 Sheets-Sheet 1

FIG. 1.



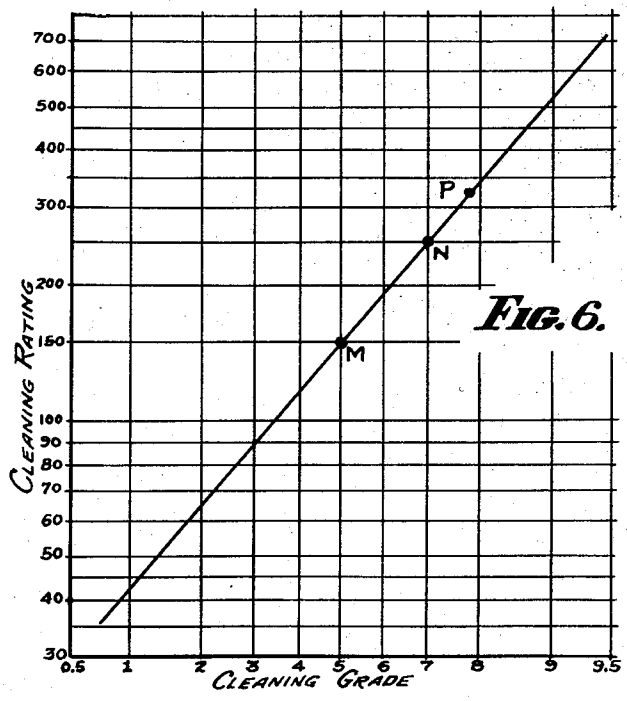


FIG. 6.

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CALCIUM PYROPHOSPHATE ABRASIVE AND DENTIFRICE CONTAINING THE SAME

Filed Aug. 20, 1956 2 Sheets-Sheet 2

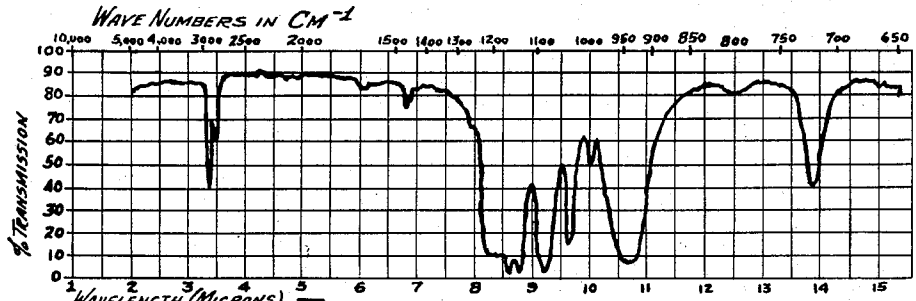


FIG. 2.

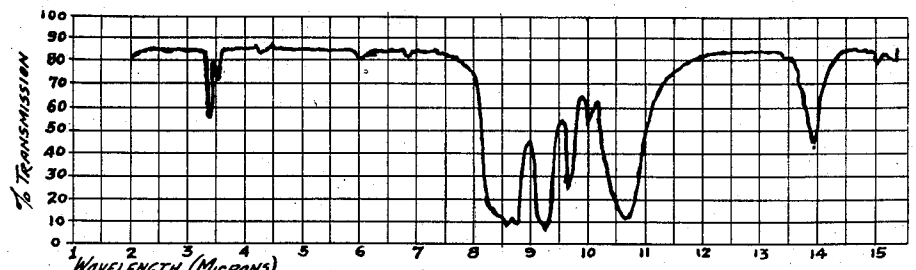


FIG. 3.

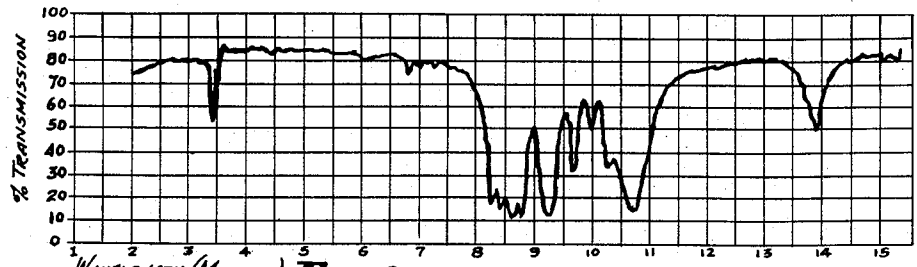


FIG. 4.

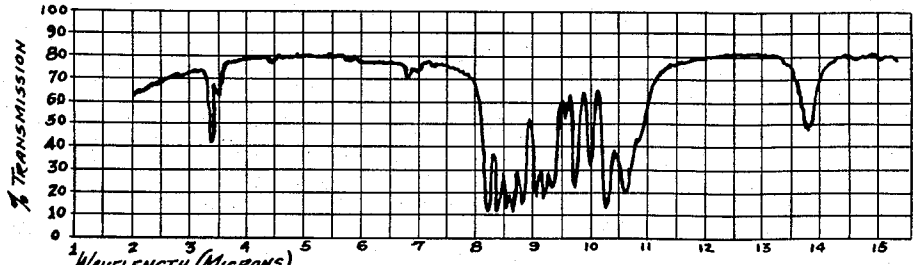


FIG. 5.

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United States Patent Office 2,876,168 Patented Mar. 3, 1959

2,876,168

CALCIUM PYROPHOSPHATE ABRASIVE AND DENTIFRICE CONTAINING THE SAME

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Application August 20, 1956, Serial No. 604,972

7 Claims. (Cl. 167—93)

This invention relates to dentifrice abrasive materials and to methods for their preparation. More particularly, it relates to particles of heat-treated calcium phosphates which are capable of satisfactorily cleaning teeth without causing a large amount of abrasion of tooth dentin. It further relates to dentifrices in which these abrasive are incorporated.

In cleaning the teeth with a toothbrush, it is customary to add to the toothbrush some cleaning material such as a toothpaste or a toothpowder. One of the components of such paste or powder is desirably an abrasive material which cuts through the surface films formed on the teeth and removes adherent stains. Materials commonly used for this purpose include precipitated chalk, dicalcium orthophosphate, calcium carbonate, hydrated alumina, finely powdered pumice, and finely divided silica.

One of the problems in choosing a suitable dentifrice abrasive is the selection of a material which will clean the teeth in a satisfactory manner but which will not remove substantial amounts of tooth dentin. Tooth dentin is frequently found exposed at the surface of the teeth near the gum line, particularly where the gums have receded. The abrasion of tooth dentin by an abrasive is much greater than the abrasion of tooth enamel by the same abrasive, i. e., 10 to 100 times. Consequenly, the enamel abrasion is considered to be of minor importance when compared with dentin abrasion, and the amount of dentin abrasion is used as a criterion in the selection of suitable dental abrasives.

It has now been found that certain calcium phosphates will clean teeth to a greater degree without a corresponding increase in dentin abrasion than has been possible heretofore when the well-known prior art dentifrice abrasives have been used, and it is one of the primary objects of this invention to provide such abrasives.

A further object of this invention is to provide dentifrices containing such abrasives.

Other objects and advantageous features will be apparent from the following detailed description and from the drawings in which

Figure 1 represents a graph demonstrating the abrasion values and cleaning grades of various dental abrasives. These abrasives are identified in the specification by the corresponding numbers,

Figures 2 to 5 show four infrared absorption spectra for various calcium pyrophosphate abrasives, and

Figure 6 shows a representative chart for determining the cleaning grade of an abrasive.

In general, the abrasives of this invention are formed by a controlled dehydration of dicalcium orthophosphate dihydrate ($CaHPO_4 \cdot 2H_2O$) in which the dihydrate is heated to a temperature within the range of from 500° C. to 700° C., the said heating being carried out at an average rate of not less than 50° C. per minute, and, in the temperature range of from 100° to 300° C., at a rate not less than 60° C. per minute, the calcium pyrophosphate formed by this heating step having a cleaning grade

of more than 6.5, and a dentin abrasion value not exceeding 600.

The preparation of calcium pyrophosphate by the heat treatment of dicalcium orthophosphate dihydrate and the use of such calcium pyrophosphate is disclosed in the copending application of Nebergall, Serial No. 366,867, filed July 8, 1953, but the application does not teach the rapid heating to a controlled temperature which is necessary to produce the abrasives of this invention.

In order to identify the composition and to determine the efficacy of the abrasives of this invention, a number of tests have been devised. These are described in detail hereafter, and it will suffice to say here that in accordance with the scales of measurement defined, a dentin abrasion value above 700, shown by the line AB of Figure 1 is considered unsatisfactory. The best cleaning grade for commercial prior art abrasives having a dentin abrasion value of not over 700 is 7, shown by line CD of Figure 1. The calcium pyrophosphate abrasives of this invention have values appearing within the area bounded by lines EF and EG.

At this point it seems desirable to define with some particularity the crystalline phases of calcium pyrophosphate which are relevant to the present discovery and to the methods by which they may be formed. The presence of gamma and beta phases of calcium pyrophosphate can be detected by means of X-ray diffraction patterns, but such patterns cannot furnish a reliable indication of the relative quantities of the phases in mixtures. An identification of the relative quantities of these phases can be found by infrared absorption spectra, as will hereinafter be set forth, although the infrared does not fully distinguish the abrasives of this invention from other materials of the same composition but which lack the high cleaning power of the abrasives of this invention.

As has been previously stated, the starting material for forming the abrasives of this invention is dicalcium orthophosphate dihydrate. This material is commercially available or it may be prepared by adding a lime slurry to orthophosphoric acid until the slurry has a pH of 4.5 while maintaining the temperature below 45° C. The precipitate which is formed (dicalcium orthophosphate dihydrate) is filtered and dried.

When dicalcium orthophosphate dihydrate is heated to a temperature within the range from about 100° to 300° C., water of hydration is driven off, and anhydrous dicalcium orthophosphate is formed. When anhydrous dicalcium orthophosphate is heated to a temperature above about 300° C., water of constitution is removed, resulting in the formation of calcium pyrophosphate ($Ca_2P_2O_7$). When the temperature does not exceed about 500° C., the calcium pyrophosphate will be in the gamma phase. Figure 2 represents an infrared absorption spectrum for substantially entirely gamma-phase calcium pyrophosphate. The substantially pure gamma-phase calcium pyrophosphate may be identified particularly by an infrared absorption maximum at a wavelength expressed as 935 reciprocal centimeters. Substantially pure gamma-phase calcium pyrophosphate has a cleaning grade which is not superior to commercially available prior art dentifrice abrasives.

When gamma-phase calcium pyrophosphate is heated to a temperature exceeding about 500° C., the gamma-phase calcium pyrophosphate will gradually convert to beta-phase calcium pyrophosphate. The presence of about 3% beta-phase calcium pyrophosphate will cause the characteristic infrared absorption maximum which appears at a wavelength corresponding to 935 reciprocal centimeters in pure gamma-phase calcium pyrophosphate to shift to a lower wavelength. Increasing amounts of beta-phase calcium pyrophosphate will cause a further shift until the infrared absorption maximum finally ap-

pears at a wavelength corresponding to 940 reciprocal centimeters. This is illustrated by Figure 3, which is an infrared absorption spectrum for a sample containing 19% beta-phase calcium pyrophosphate, the balance being substantially gamma-phase calcium pyrophosphate. For purposes of this invention, an infrared absorption maximum at 937 reciprocal centimeters indicates a composition containing about 10% beta-phase calcium pyrophosphate, the balance being substantially in the gamma phase. The presence of beta-phase calcium pyrophosphate tends to cause an increase in the dentin abrasion values of calcium pyrophosphates.

A further increase in the beta-phase content of calcium pyrophosphate will result in the appearance of an additional infrared absorption maximum at a wavelength corresponding to 970 reciprocal centimeters. This is shown by Figure 4, which represents an infrared absorption spectrum for a sample containing about 24% beta-phase calcium pyrophosphate, the balance being substantially gamma-phase calcium pyrophosphate.

When the amount of beta-phase calcium pyrophosphate exceeds about 50%, the dentin abrasion value will exceed 600, and as the percentage of beta-phase increases, the dentin abrasion value will also increase. The presence of about 50% of beta-phase calcium pyrophosphate will be shown when the infrared absorption maximum at a wavelength of 970 reciprocal centimeters is of the same optical density as the absorption maximum at 940 reciprocal centimeters. The absorption maximum at 970 reciprocal centimeters will be greater than that at 940 reciprocal centimeters when the calcium pyrophosphate is more than 50% in the beta phase. This is illustrated by Figure 5, which shows an infrared absorption spectrum for a sample containing 51% beta-phase calcium pyrophosphate, the balance being substantially gamma-phase calcium pyrophosphate.

It has now been found that when calcium pyrophosphate is prepared by heating dicalcium orthophosphate dihydrate rapidly to a temperature of from 500° C. to 700° C. at a rate of heating such that the average rate of heating is not less than 50° C. per minute and the rate of heating in the range of from 100° C. to 300° C. is not less than 60° C. per minute, and when the heating within the temperature range from 500° C. to 700° C. is continued until the composition contains at least 10% beta-phase calcium pyrophosphate but not more than 50% beta-phase calcium pyrophosphate, the material formed thereby will have a cleaning grade of 6.5 or more. It has been further found that when the rate of heating from 100° to 300° C. is less than 60° C. per minute or if the average heating rate to 500° C. is less than 50° C. per minute, the cleaning grade will always be less than 6.5.

While not intending to be bound by any particular theory as to the changes in crystalline phase of the dicalcium orthophosphate dihydrate, it is believed that when the temperature of the dicalcium orthophosphate dihydrate is increased at a rate of heating of 60° C. per minute or more, water of constitution is driven off simultaneously with water of hydration, so that the structure of a particle produced by such rapid heating consists of a center core formed from substantially pure gamma-phase calcium pyrophosphate and that the beta-phase calcium pyrophosphate is concentrated at the surface.

In order that the reader may be oriented to the cleaning and abrasion values of commercially available prior art abrasives, the following values determined in accordance with the standardized methods later defined are given. Table I lists representative prior art dentifrice abrasives, all of which were tested in slurries having concentrations of 25.0 grams per 50 cc. of water. The sample numbers refer to their values plotted on Figure 1. Sample No. 3 is a mixture of Samples Nos. 1 and 2.

TABLE I

Sample No.	Abrasive	Dentin Abrasion Value	Cleaning Grade
1	Precipitated anhydrous dicalcium orthophosphate.	1010	9.0
2	Precipitated dicalcium orthophosphate dihydrate.	255	5.0
3	80% (2) + 20% (1)	700	7.0
4	Calcium carbonate	600	5.0

Sample No. 1 has too high a dentin abrasion value to be satisfactory for use in a toothpaste. Samples Nos. 2, 3, and 4 represent dentifrice abrasives having properties which provide cleaning to a lesser degree than the abrasives of this invention.

Table II shows typical differences in dentin abrasion values and cleaning grades for abrasives formed from samples of dicalcium orthophosphate dihydrate which have been subjected to various rates of heating and final heating temperatures. Each of these abrasives was made by placing 300 grams of commercial grade dicalcium orthophosphate dihydrate in a stainless steel tray. The material was arranged in an even level in the tray and the tray was placed in the center of a Globar furnace. Each of the samples remained in the furnace for a total time of two hours. Each sample was then removed, cooled in air, and bottled. The sample numbers correspond to the numbered points in Figure 1.

TABLE II

Sample No.	Final Heating Temp. (°C.)	Rate of Heating 103°–200° C. (°C./min.)	Dentin Abrasion Value	Cleaning Grade	$Ca_2P_2O_7$ Phase (present)	
					Beta	Gamma
5	375	6	204	5.1	-------	62 [1].
6	500	37	304	5.9	14	Balance.
7	500	60	283	6.9	14	Do.
8	600	18	281	5.4	18	Do.
9	600	35	325	5.6	16	Do.
10	600	53	259	5.8	16	Do.
11	600	72	428	7.1	[2]	[2]
12	600	103	296	7.6	16	Balance.
13	650	91	469	7.1	16	Do.
14	650	106	359	9.0	16	Do.
15	750	135	750	5.2	51	Do.

[1] The balance was anhydrous dicalcium orthophosphate.
[2] Not measured.

As can be seen from Table II, heating dicalcium orthophosphate dihydrate to a final temperature less than about 500° C. forms an abrasive having an undesirably low cleaning grade. When the final heating temperature exceeds about 700° C., an abrasive is produced which has an undesirably high dentin abrasion value. Table II further shows that a rate of heating less than about 60° C. per minute in the range from 100° C. to 300° C. does not form an abrasive having a cleaning grade as great as about 6.5. However, when the rate of heating is at least 60° C. per minute in the range from 100° C. to 300° C. and the final temperature is between 500° C. and 700 C., the abrasives produced after a total heating time of about two hours will have a cleaning grade of at least about 6.5 and a dentin abrasion value of not more than 600. Samples Nos. 7, 11, 12, 13, and 14 are representative of such abrasives and are examples of the invention.

The total heating time required to form calcium pyrophosphates of this invention may be as short as 10 minutes. Longer periods of time up to 10 hours or more can be used. However, suitable heating times can best be determined by infrared analyses of the calcium pyrophosphates produced by the heat treatment.

The size of the particles after heat treatment will be approximately the same as the size of the particles of the dicalcium orthophosphate dihydrate starting material. It is preferred that the dicalcium orthophosphate dihy-

drate have a median particle size of from 6 to 10μ and comprise substantially no particles less than 3μ. As long as the particles to be heat-treated are within this size range, very little difference is noted in abrasion values or cleaning grade for the calcium pyrophosphate produced if it is in the proper crystalline phases.

If a large number of the particles have diameters greater than 20μ, they may cause a gritty sensation in the mouth when they are incorporated in a dentifrice and may be undesirable. Particles smaller than 3μ have too low a cleaning grade to be a satisfactory dentifrice abrasive. For best results, at least 80% of the particles should have diameters ranging from 3μ to 20μ.

The calcium pyrophosphate abrasives of this invention can be incorporated in a wide variety of toothpastes and tooth powders.

In preparing toothpastes, it is necessary to add some thickening material. Suitable thickeners include natural gums, such as gum karaya, gum arabic, and gum tragacanth; seaweed derivatives, such as Irish moss and alginates; and water-soluble salts of cellulose ethers, such as sodium carboxymethyl cellulose and sodium carboxymethyl hydroxyethyl cellulose. Improvements in texture may also be provided by including an additional material such as colloidal magnesium aluminum silicate.

Toothpastes conventionally contain sudsing agents. Suitable sudsing agents include, but are not limited to, water-soluble alkyl and alkyl ether sulfates and sulfonates having alkyl groups of from 8 to 18 carbon atoms, water-soluble salts of sulfonated monoglycerides of fatty acids having from 10 to 18 carbon atoms, salts of fatty acid amides of taurines such as sodium-N-methyl-N-palmitoyl tauride, and salts of fatty acid esters of isethionic acid. Mixtures of two or more sudsing agents can also be used.

Calcium pyrophosphate may be the sole abrasive in the toothpaste, or may be combined with other conventional abrasives as listed heretofore.

It is also desirable to include some humectant material in a toothpaste to keep it from hardening. Materials commonly used for this purpose include glycerine, sorbitols, and other polyhydric alcohols.

Toothpastes may additionally include small amounts of flavorings, such as oils of wintergreen and peppermint, and sweetening agents such as saccharine, dextrose, and levulose.

Suitable toothpastes containing the calcium pyrophosphates of this invention may be made from the following range of components. It is to be understood that these formulations are given by way of example, and that certain proportions of specific materials may be necessary to provide optimum properties. Further, it is to be understood that the toothpaste components are not to be limited to those listed but may include other ingredients known to those skilled in the art.

Toothpaste formulations

Abrasive	10% to 60%.
Thickening agent	0.25% to 5%.
Humectants	0% to 40%.
Sudsing agents	0.25% to 5%.
Flavoring, Sweetening	To taste.
Water	Balance.

The following illustrates the composition of a satisfactory toothpaste containing calcium pyrophosphates of this invention:

	Percent
Abrasive	45.00
Carboxymethyl cellulose	1.20
Glycerine	10.00
Sorbitol	20.00
Sudsing agent	1.51
Saccharine	0.12
Flavoring	0.85
Water	21.32

The abrasive used in this toothpaste was made by heating dicalcium orthophosphate dihydrate to a temperature of 620° C. at an average rate of 65° C. per minute and at a rate of about 82° C. per minute between 100° and 300° C. The sample was maintained at a temperature of 620° C. for about 4 hours. The calcium pyrophosphate contained 19% beta-phase calcium pyrophosphate, the balance being substantially in the gamma phase. The abrasive had a cleaning grade of 7.2 and a dentin abrasion value of 395, and is shown as point No. 16 of Figure 1. The infrared absorption spectrum for this abrasive is shown in Figure 3.

A satisfactory toothpaste embodying the calcium pyrophosphate listed as Sample No. 14 in Table II can be made with the following composition:

	Percent
Abrasive	40.00
Irish moss	1.50
Glycerine	25.00
Sudsing agents	1.25
Saccharine	0.12
Flavoring	1.00
Water	Balance

The toothpastes may be adapted for use in collapsible tubes, in aerosol-type dispensers, or by other means.

If the calcium pyrophosphates of this invention are to be incorporated in a tooth powder, the following range of formulations will provide a satisfactory dentifrice:

Tooth powder formulations

Sudsing agent	0% to 5%
Flavoring, Sweetening	To taste.
Abrasive	Balance.

An example of a very satisfactory toothpowder which contains the calcium pyrophosphate listed as Sample No. 12 of Table II is as follows:

	Percent
Abrasive	95.50
Sudsing agent	3.00
Flavoring	1.25
Saccharine	0.25

Dentifrices, both in paste and powder form, may include additional materials which will provide desirable properties. An example of such a material is stannous fluoride. The following composition is illustrative of such a dentifrice:

	Percent
Abrasive	40.00
Sudsing agent	1.51
Glycerine	10.00
Sorbitol	20.00
Carboxymethylcellulose	1.10
Magnesium aluminum silicate	0.40
Stannous fluoride	0.40
Saccharine	0.12
Flavoring	0.85
Coloring	0.47
Water	Balance

A suitable abrasive for this composition is one such as Sample No. 13 of Table II.

Additional examples of material which may be added to the dentifrices of this invention include, but are not limited to, sarcosinates, fluorine-containing compounds, quaternary ammonia compounds, chlorophyll, sodium dehydroacetates, sodium lauryl sulfate, tyrothrycin, penicillin, and hexachlorophene.

The method for determining dentin abrasion values and cleaning grades of abrasives are as follows:

Dentin abrasion

The dentin portions are separated from human central incisors having not more than minor imperfections. These dentin portions are exposed to neutron radiation whereby some of the phosphate content is converted to P^{32}. The irradiated tooth portions are mounted in Woods metal and submerged in a slurry of the abrasive material to be tested. A toothbrush is so arranged that it can be moved back and forth across the surface of the submerged portion of tooth or dentin, and the pressure of this toothbrush is adjusted to 150 grams. The tooth dentin is subjected to the brushing action for a given number of strokes, and removed from the slurry. The radio-activity of the slurry is then counted by means of standard radioactivity counting equipment. An equivalent piece of dentin, irradiated concurrently with the dentin portions to be brushed, is weighed and then dissolved in hydrochloric acid. The radioactivity is counted. Using this as a standard, the amount of tooth dentin removed during the brushing can be determined by comparing the count of the brushing slurry with the count of this standard.

A standard slurry for measuring dentin abrasion is made from massive calcite ($CaCO_3$). The calcite is ground in a hammer mill to a median particle diameter of about 23μ. The particles are then ball-milled to a median particle size of about 13.3μ, and should have approximately the particle size distribution as set forth in the following Table III.

TABLE III

Particle diameter (μ):	Wt. percent smaller
3.0	25
5.5	30
7.6	35
9.6	40
11.4	45
13.3	50
17.4	60
24.5	75
30.0	85

The concentration of the standard slurry is 12.5 g. per 50 cc. of water. Slurries for evaluating the abrasives are made at a concentration of 25 g. per cc. of water.

To determine the abrasion value of an abrasive, a portion of irradiated tooth dentin is first brushed with the calcite slurry. The same portion of dentin is then cleaned with water and brushed with a slurry of the abrasive to be tested. The dentin is again cleaned and brushed with the calcite slurry. Each of these slurries is counted and the average amounts of dentin removed per 100 double strokes (back and forth) during the total amount of brushing with the slurries of calcite and with the abrasive being tested are calculated. The amount per 100 double strokes removed by the calcite slurry is given an arbitrary value of 600. The factor required to effect the conversion of the number of micrograms of dentin removed to this value of 600 is multiplied times the average amount of dentin removed by brushing 100 double strokes with the abrasive being tested. The product is the abrasion value of the abrasive.

As an example, if the average amount of dentin removed by 100 double brushing strokes in a calcite slurry is 100 micrograms, the conversion factor to obtain an abrasion value of 600 is

$$\frac{600}{100}$$

or 6.0. Using the same portion of tooth dentin, if 100 double brush strokes in a slurry of calcium pyrophosphate removes an average of 75 micrograms, multiplying this weight by the conversion factor (6.0) will give an abrasion value for the calcium pyrophosphate of 450.

Cleaning

Two standard aqueous slurries are used to determine the cleaning grade of an abrasive. One slurry is made with 25 g. of dicalcium phosphate dihydrate per 50 cc. of water. The commercially available dentifrice grade of dicalcium phosphate dihydrate is suitable, but it should be milled to a particle size distribution approximately as shown in the following Table IV.

TABLE IV

Particle diameter (μ):	Wt. percent smaller
26.4	90
21.8	80
17.3	70
13.2	60
9.6	50
6.4	40
4.0	30
2.3	20

The second standard slurry is made from a mixture of 80% dicalcium orthophosphate dihydrate and 20% anhydrous dicalcium orthophosphate in a concentration of 25 g. per cc. of water. The dicalcium orthophosphate dihydrate is the same as that used in the first standard slurry. The anhydrous dicalcium orthophosphate is the commercially available grade which should have a particle size distribution approximately as shown in the following Table V.

TABLE V

Particle diameter (μ):	Wt. percent smaller
44.0	90
37.0	80
31.0	70
26.0	60
21.0	50
17.0	40
12.8	30
7.8	20

White urea formaldehyde blocks having a surface measuring 10 mm. x 12 mm. are ground smooth. The blocks are washed and dried and then exposed to an infrared bulb for at least 10 minutes to completely dry the surfaces. On this surface is placed one drop of lacquer thinner (Duco No. 3661, made by the DuPont Company) using a commercial eye-dropper. The drop is allowed to spread over the surface of the block. A mixture is made of two parts of the lacquer thinner and one part of black lacquer (FoMoCo—Color Patch, Black, M–1724, made by the Ford Motor Company). Four drops of this mixture are placed on the surface of the block, using a hypodermic syringe and a #23 needle. These drops are allowed to spread, and the blocks are air-dried and then placed under an infrared bulb and dried for at least 20 minutes more. The weight of the lacquer coating should be 0.0020 ± 0.0002 gram.

The blocks are inserted in abrasive slurries and brushed by toothbrushes in a manner similar to that used in the determination of the abrasion values. The blocks are brushed in increments of 500 strokes each, and the percent reflectance of the blocks are measured after each brushing increment using a modified Photovolt Reflectance meter. For each abrasive being tested, a curve is plotted, using as one coordinate the number of strokes and as the other coordinate the measured percent reflectance. From this curve, a value representing the number of strokes to get 30% gain in reflectance is read, and from this number of strokes is calculated the percent gain in reflectance per stroke. This percent gain in reflectance per stroke is multiplied by 10,000 to obtain the cleaning rating. A cleaning rating is calculated for

each of the standard abrasives each time a determination is made of an abrasive being tested.

The cleaning grade is determined by the use of Logarithmic Probability Graph Paper No. 3128, designed by Hazen, Whipple and Fuller, and made by the Codex Book Company, Inc., Norwood, Massachusetts, and shown in Figure 6. Cleaning grade values of 1 to 9 are assigned to the printed 10 to 90 values on the probability scale. The logarithmic scale is used to plot the cleaning rating values, assigning a value of 10 to the origin. On this chart, a point is plotted so that the cleaning rating of dicalcium phosphate dihydrate has a cleaning grade of 5. A second point is plotted giving a cleaning grade of 7 to the mixture of 80% dicalcium phosphate dihydrate and 20% anhydrous dicalcium phosphate. A straight reference line is drawn through these two points. The cleaning grade of any other dentifrice abrasive can be read from this chart by selecting the point representing the intersection of the cleaning rating value and the reference line, and then reading the value of this intersection point on the cleaning grade scale.

As an example, the cleaning rating of a standard slurry of dicalcium phosphate dihydrate was found to be 150. Assigning a cleaning grade of 5 to this abrasive, it is plotted on Figure 6 as point M. The second standard abrasive mixture containing 80% dicalcium orthophosphate dihydrate and 20% anhydrous dicalcium orthophosphate was found to have a cleaning rating of 250. Assigning a cleaning grade of 7 to this second standard abrasive, it is plotted as point N in Figure 6. A straight line is drawn through these two points. By following the brushing and calculating procedure hereinbefore set forth, a calcium pyrophosphate is found to have a cleaning rating of 320. Referring to the line of Figure 6, it can be seen that the cleaning grade of the sample abrasive is 7.8 (point P).

This test has shown very good correlation with clinical tests in which the cleaning is directly measured by inspection of teeth in the human mouth. In addition, it has a sensitivity to variations in cleaning power which is greater than that which can be attained in clinical cleaning tests.

What is claimed is:

1. The method of making a calcium pyrophosphate suitable for use as a dental abrasive which comprises the steps of heating dicalcium orthophosphate dihydrate to a temperature within the range from 500° C. to 700° C., the said heating being carried out at an average rate of not less than 50° C. per minute, and in the temperature range of from 100° to 300° C., at a rate of not less than 60° C. per minute, and maintaining the resulting product at a temperature within the range from 500° C. to 700° C. until at least 10% but not more than 50% is beta-phase calcium pyrophosphate, the balance being substantially gamma-phase calcium pyrophosphate.

2. The method according to claim 1, wherein the dicalcium orthophosphate dihydrate has a median particle size of from 6 to 10μ and comprises substantially no particles less than 3μ.

3. A dental abrasive comprising from 10% to 50% beta phase calcium pyrophosphate, the balance being substantially gamma-phase calcium pyrophosphate, said abrasive having a cleaning grade of not less than 6.5 and a dentin abrasion value not exceeding 600 when tested as set forth in the specification, said abrasive being prepared by heat treatment of dicalcium orthophosphate dihydrate.

4. A dental abrasive according to claim 3, wherein the calcium pyrophosphate is in the form of particles at least 80% of which have diameters ranging from 3μ to 20μ.

5. A dentifrice comprising a sudsing agent and an abrasive, said abrasive comprising particles of calcium pyrophosphate, from 10% to 50% of said calcium pyrophosphate being in the beta phase and the balance being substantially in the gamma phase, said abrasive having a cleaning grade of not less than 6.5 and a dentin abrasion value not exceeding 600 when tested as set forth in the specification, said abrasive being prepared by heat treatment of dicalcium orthophosphate dihydrate.

6. A dentifrice according to claim 5 wherein at least 80% of the particles of calcium pyrophosphate have diameters ranging from 3μ to 20μ.

7. A dentifrice comprising a sudsing agent and an abrasive, said abrasive comprising a calcium pyrophosphate formed by heating dicalcium orthophosphate dihydrate to a temperature within the range from 500° to 700° C., the said heating being carried out at an average rate of not less than 50° C. per minute and, in the temperature range of from 100° to 300° C., at a rate of not less than 60° C. per minute, and maintaining the resulting product at a temperature within the range from 500° C. to 700° C. until at least 10% but not more than 50% is beta-phase calcium pyrophosphate, the balance being substantially gamma-phase calcium pyrophosphate.

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