Oct. 10, 1961 R. W. BROGE 3,003,919

ALUMINA ABRASIVE MATERIALS

Filed June 22, 1956 2 Sheets-Sheet 1

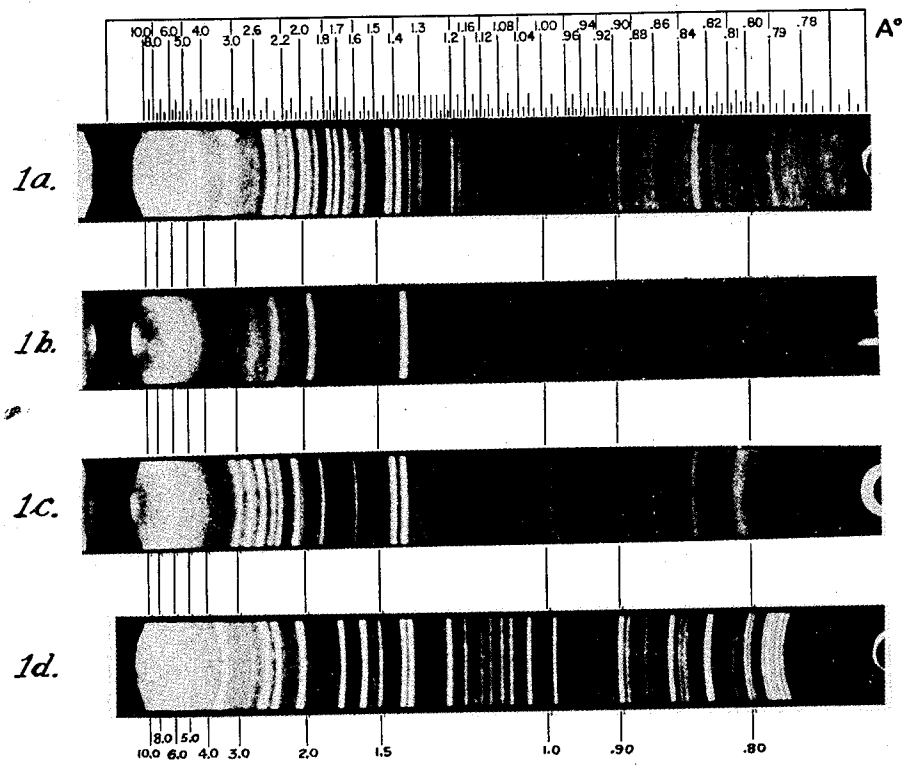


FIG. 1.

INVENTOR.
ROBERT W. BROGE,
BY
Allen & Allen
ATTORNEYS.

Oct. 10, 1961 R. W. BROGE 3,003,919

ALUMINA ABRASIVE MATERIALS

Filed June 22, 1956 2 Sheets-Sheet 2

FIG. 3.

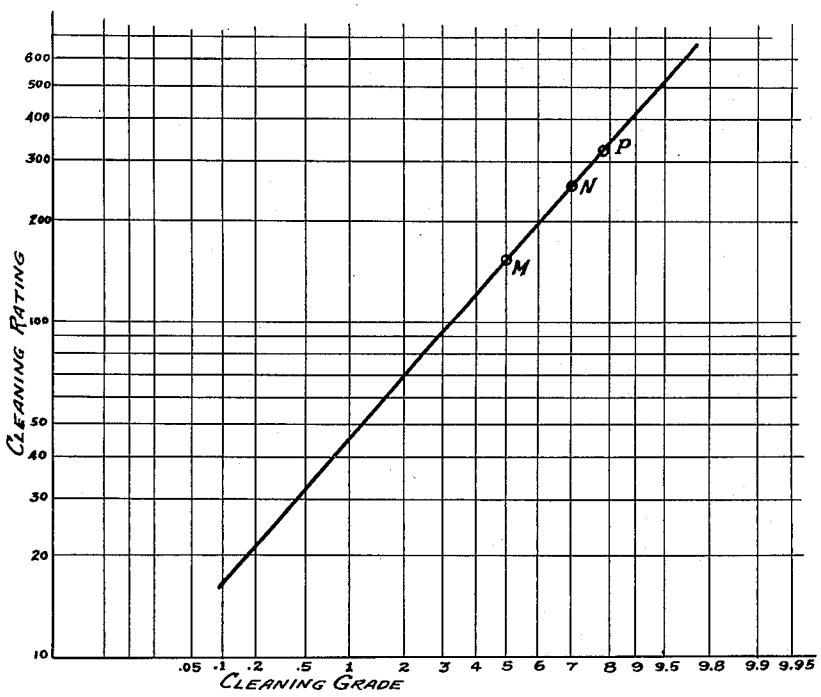
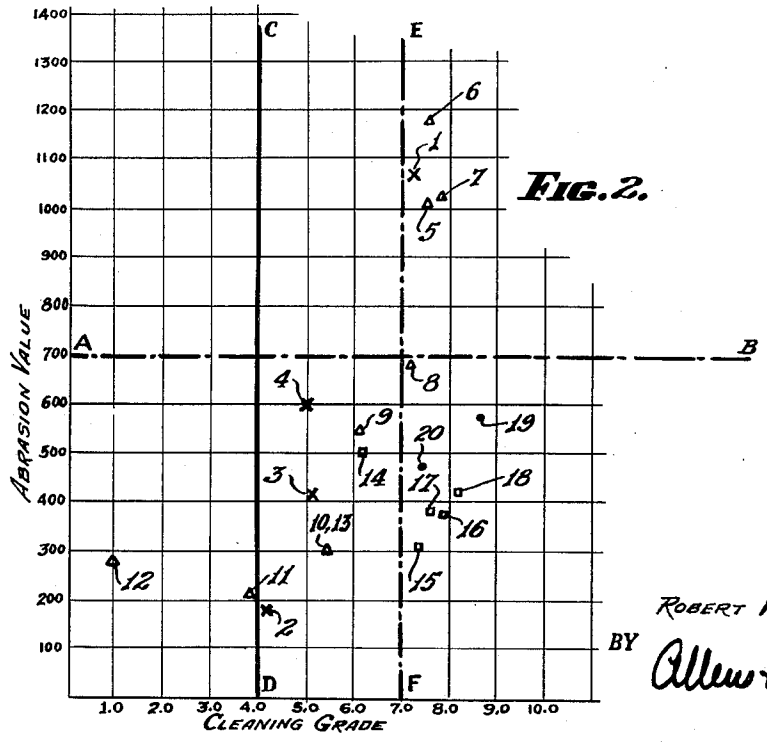


FIG. 2.



INVENTOR.
ROBERT W. BROGE,
BY Allen + Allen
ATTORNEYS.

United States Patent Office 3,003,919 Patented Oct. 10, 1961

3,003,919

ALUMINA ABRASIVE MATERIALS

Robert W. Broge, Mount Healthy, Ohio, assignor to The Procter & Gamble Company, Cincinnati, Ohio, a corporation of Ohio

Filed June 22, 1956, Ser. No. 593,253
4 Claims. (Cl. 167—93)

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

In cleaning the teeth with a toothbrush, it is customary to add to the brush some cleaning material such as a toothpaste or a tooth powder. 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 the adherent stains. Materials commonly used for this purpose include precipitated chalk, calcium phosphates, calcium carbonate, hydrated alumina, finely powdered pumice, and finely divided silica.

Polishing of teeth can occur when an abrasive planes off irregularities of the enamel tooth surfaces. The resulting surfaces appear to the eye as highly polished planes.

Some of the dentifrice abrasives listed above, such as precipitated chalk, dicalcium orthophosphate, calcium carbonate, and hydrated alumina, have no measurable effect in polishing the enamel surfaces of teeth. Other abrasive materials such as finely powdered pumice and finely divided silica do polish the enamel surfaces of the teeth but also abrade and 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. Consequently, 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 by the process of this invention, abrasive materials can be prepared which will clean teeth and will also impart a high polish to them but which will not unduly abrade tooth dentin. In addition, certain of the abrasive materials within the scope of this invention will clean the teeth to a greater degree, without a corresponding increase in dentin abrasion, than has been possible heretofore when prior art dentifrice abrasives have been used.

Accordingly, it is one of the objects of this invention to provide improved abrasives and methods for making such abrasives.

Another object is to provide abrasive materials which will impart a high polish to the teeth.

A further object is to provide abrasive materials which will clean teeth more thoroughly than has formerly been possible without causing excessive abrasion of tooth dentin.

Other objects and advantageous features will be apparent from the following specification and from the drawings in which:

FIGURE 1*a* represents an X-ray diffraction pattern for alpha alumina trihydrate,

FIGURE 1*b* represents an X-ray diffraction pattern for gamma-phase alumina,

FIGURE 1*c* represents an X-ray diffraction pattern for kappa-phase alumina,

FIGURE 1*d* represents an X-ray diffraction pattern for alpha-phase alumina,

FIGURE 2 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, and

FIGURE 3 represents a representative chart for determining the cleaning grade of an abrasive.

In general, the process of this invention comprises the controlled dehydration of gibbsite (alpha alumina trihydrate) to produce a dehydrated alumina mixture containing a desirable amount of alumina in the kappa phase and possessing improved properties as a dental abrasive. The innvention is, of course, described in greater detail below, but at this point it seems desirable to define with some particularity the crystalline phases of alumina relevant to the present discovery.

The diffraction pattern for gibbsite (alpha alumina of alumina may vary, depending upon the investigator. For the purpose of this invention, certain crystalline forms of hydrated and unhydrated alumina are identified by means of distinctive patterns obtained by X-ray diffraction.

The diffraction pattern for gibbsite (alpha alumina trihydrate) is shown in FIGURE 1*a* and reveals strong lines corresponding to interplanar spacings of 2.03 A. and 2.44 A. Gibbsite occurs in nature as a principal constituent of bauxite. It is commercially prepared by the Bayer process in which bauxite is digested with a hot caustic soda solution to put the alumina in solution as sodium aluminate, separating the insoluble residue, and seeding and cooling to form crystals of gibbsite.

As gibbsite is heated to the dehydrating temperature within the range from about 500° C. to about 800° C., water is driven off from the structure, and gamma-phase alumina is formed. An X-ray diffraction pattern for gamma-phase alumina is shown in FIGURE 1*b*, which reveals strong diffraction lines at spacings of 1.39 A. and 1.98 A. The presence of gamma-phase alumina in the heat-treated abrasive increases the cleaning grade, but an excess of gamma alumina will cause too large an amount of dentin abrasion.

Continued heating at temperatures below about 900° C. will cause very little change in the crystalline phase of the gamma alumina. However, if the alumina is heated to a temperature higher than about 900° C. but not higher than about 1050° C., it will be transformed into kappa-phase alumina. An X-ray diffraction pattern for kappa-phase alumina is shown in FIGURE 1*c* which reveals, in addition to the diffraction lines characteristic of gamma-phase alumina, strong diffraction lines at spacings of 1.43 A. and 2.79 A. It has been found that some of the alumina formed in this temperature range may be in what is known as the "theta" phase. This phase is described in "Technical Paper No. 10, Alumina Properties," Allen S. Russell, Aluminum Company of America, 1953, on pages 8 and 9. In aluminas made by the process of this invention, alumina is never formed in this phase alone, but appears in combination with larger amounts of kappa-phase alumina. The presence of theta-phase alumina can be detected by a stronger diffraction line at a spacing of 2.73 A. than is formed by the pure kappa-phase alumina, shown in FIGURE 1*c*. Although

the amount of such theta-phase alumina in a sample is determined separately, as hereinafter described, the effect of theta-phase alumina on the performance of the alumina abrasives of this invention does not appear to differ from that of kappa-phase alumina. Aluminas in these two phases are to be considered equivalents for the purposes of this invention, and all crystalline aluminas possessing this characteristic diffraction pattern are intended to be hereinafter included in the term "kappa-type alumina." The presence of an excessive amount of kappa-type alumina in the abrasive tends to lower the cleaning grade.

If the kappa-phase alumina is heated to a temperature above about 1050° C., it will be transformed into alpha-phase alumina. An X-ray diffraction pattern for alpha-phase alumina is shown in FIGURE 1*d*, which reveals strong diffraction lines at spacings of 1.60 A. and 2.08 A. The presence of a small amount of alpha alumina in the abrasive will decrease the dentin abrasion, but too large an amount of alpha alumina will tend to lower the cleaning grade and increase the enamel abrasion beyond a safe level.

It has been found that the X-ray diffraction patterns of different samples of alumina prepared by the process of this invention may vary in intensity, although the spacings of the strong diffraction lines will be identical. This is caused by the presence of non-crystalline alumina or alumina having poorly crystallized or strained crystals which alter the absolute line intensities, background intensities, and line shapes of the diffraction patterns. Any of such non-crystalline or poorly crystallized aluminas are intended to be encompassed by the term "amorphous alumina."

While not intending to be bound by any particular theory as to the changes in crystalline structure of the alumina, it is believed that when the temperature of the gibbsite is increased at a rate of 20° C. per minute or greater during the dehydrating step, the water present in the gibbsite is driven off so quickly and with such force that the crystalline structure is badly strained, resulting in the formation of a substantial amount of amorphous alumina during the subsequent heating in the phase conversion temperature range.

In order to identify the composition and 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 2, and a cleaning grade below 4, shown by the line CD of FIGURE 2, are considered unsatisfactory. The best cleaning grade for prior art abrasives having reasonable dentin abrasion is 7, shown by the line EF of FIGURE 2. Polishing values are scaled from 0 to 4, the higher values denoting better polishing characteristics.

In order that the reader may be oriented to the cleaning, abrasive, and polishing 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 dentrifice abrasives, all of which were tested in slurries having concentrations of 12.5 g. per 50 cc. of water. The sample numbers refer to their values plotted on FIGURE 2. Sample No. 3 is a mixture of samples Nos. 1 and 2.

TABLE I

Sample No.	Abrasive	Dentin Abrasion Value	Cleaning Grade	Polishing Value
1	Anhydrous dicalcium phosphate	1,076	7.2	0
2	Dicalcium phosphate dihydrate	192	4.1	0
3	86% (2)+14% (1)	405	5.2	0
4	Calcium carbonate	600	5.0	0

Sample No. 1 has too high a dentin abrasion value to be satisfactory for use in a toothpaste. Samples 2, 3, and 4 represent dentifrice abrasives having properties which provide cleaning which is satisfactory by prior art standards and which do not cause an undue amount of dentin abrasion. However, as shown by the last column of Table I, none of the abrasives listed have any polishing power.

With this background, the invention can now be described in somewhat greater detail.

In general, the process of this invention comprises the steps of dehydrating gibbsite (alpha alumina trihydrate) by heating it to a temperature within the range from about 500° to about 800° C., further heating the alumina thereby formed to a temperature within the phase conversion temperature range of from about 900° C. to about 1050° C., and maintaining the alumina within the said phase conversion temperature range of from about 900° C. to about 1050° C. until the alumina comprises not more than about 20% gamma alumina and not more than about 10% alpha alumina. At least 20% but not more than 90% of the alumina should be kappa-type alumina. The balance of the alumina will be substantially amorphous.

At least about one hour of heating in the phase conversion temperature range will be necessary to form the minimum desirable amount of kappa-type alumina. The heating should not be continued an excessive time or more than 90% of the aluminum may be of the kappa type. The maximum time for heating the alumina in the phase conversion temperature range will vary depending upon the temperature. In general, a longer heating time can be permitted when heating at lower temperatures, since the kappa-type alumina is formed more slowly than during heating at higher temperatures. Also, at the highest part of the phase conversion temperature range, too large an amount of alpha alumina may be formed if the heating time is too long. When the phase conversion temperature is 1000° C., the total heating time should not be more than about 10 hours.

If the temperature of the gibbsite is increased at a rate of less than 20° C. per minute during the initial dehydrating step in which the gibbsite is heated to a temperature within the range of from about 500° C. to about 800° C., it will be found that the alumina formed after subsequent heating in the phase conversion temperature range will contain more than 55% kappa-type alumina and will have a cleaning rating of at least 4 and a dentin abrasion value of not more than 700. These values are comparable to those of the best prior art dentifrice abrasives. The polishing power is far superior to that of prior art abrasives.

If the temperature of the gibbsite is increased at a rate of from 20° C. to 210° C. per minute during the initial dehydrating step, it will be found that alumina formed after the subsequent heating in the phase conversion temperature range will contain not more than 55% kappa-type alumina. The cleaning ratings of such aluminas will be not less than 7 and the dentin abrasion values will be not greater than 700. No prior art abrasives have been known which have such a large cleaning rating at an acceptable dentin abrasion value.

Table II shows typical differences in dentin abrasion values and cleaning grades which result from variations in the temperature of the final heat-treatment step after the gibbsite has been dehydrated. Each of the abrasives listed in Table II, except sample No. 5, was made by placing 150 grams of gibbsite in a 150 mm. evaporating dish. The dish was placed in a furnace preheated to 300° C., and then the furnace temperature was increased to the final heat treatment temperature at such a rate that the temperature of the sample rose about 5° to 8° C. per minute. The temperature was then maintained at this final value for two hours. Each sample was removed from the furnace, air cooled, and bottled. The

sample numbers correspond to the numbered points in FIGURE 2.

TABLE II

Sample No.	Final Heat Treatment Temp. (° C.)	Dentin Abrasion Value	Cleaning Grade	Polishing Value
5	Unheated	1,017	7.5	0
6	500	1,190	7.5	0.9
7	700	1,029	7.7	1.3
8	900	696	7.2	1.5
9	950	549	6.0	1.4
10	1,000	301	5.4	2.5
11	1,050	205	3.9	2.2
12	1,150	286	1.0	1.6

As can be seen from this table, heat treatment at a temperature less than about 900° C. produces an abrasive having an undesirably high dentin abrasion value. Heat treatment at temperatures exceeding about 1050° C. produces an abrasive with an undesirably low cleaning grade. Samples 8 to 11 represent examples of aluminas of this invention. All of the heat-treated alumina samples listed in Table II polished the enamel surfaces of teeth.

The following Table III lists further examples of aluminas of this invention and compares the properties of aluminas prepared by slow and rapid initial heating of the gibbsite. In each case, the material was further heat-treated at 1000° C. until the total time in the furnace was about two hours. The sample numbers correspond to the numbered points of FIGURE 2.

TABLE III

Sample No.	Rate of Heating to 450° C.	Dentin Abrasion Value	Cleaning Grade	Polish
13	9.0° C./min.	301	5.4	2.5
14	16.8° C./min.	507	6.2	(1)
15	20° C./min.	304	7.4	(1)
16	32.3° C./min.	374	7.7	3.8
17	120° C./min.	392	7.6	3.8
18	210° C./min.	427	8.1	(1)

[1] Polishing not measured on these samples, but previous work had shown that all anhydrous alumina polished teeth.

Although the process has been indicated as proceeding in several steps in order to more specifically define the changes in the gibbsite starting material, it is to be understood that these steps may follow each other in a continuous heating cycle without interruption. From an economic standpoint, such procedure may be highly desirable.

The size of the particles after heat treatment will be approximately the same as the size of the particles of the gibbsite starting material. It is preferred that the gibbsite 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, cleaning grades, or polishing values for the resulting alumina 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.

If the particles of gibbsite are too large, they may be ground to a desired size either before or after heat treatment.

The alumina abrasives of this invention are in the form of skeletal particles, being porous agglomerates having structural rigidity. Electron microscopy has shown that when the normal force experienced in brushing teeth is applied, these skeletal particles break down into extremely fine hard particles which tend to polish the enamel rather than to scratch it.

The alumina abrasives of this invention are very suitable for use in dentifrices. These dentifrices may be either in the form of toothpastes or 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 textures 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-polymitoyl tauride, and salts of fatty acid esters of isethionic acid. Mixtures of two or more sudsing agents can also be used.

The alumina abrasive of this invention 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 oil of wintergreen and peppermint, and sweetening agents such as saccharine, dextrose, and levulose.

Suitable toothpastes containing the alumina abrasives 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	1 part to 120 parts.
Thickening agent	0 part to 20 parts.
Humectants	0 part to 60 parts.
Sudsing agents	1 part to 10 parts.
Flavoring, sweetening	To taste.
Water	Amount necessary to form a paste.

The following illustrates the composition of a toothpaste containing an alumina abrasive of this invention:

	Percent
Abrasive	40.0
Irish moss	1.5
Glycerine	25.0
Sudsing agents	1.25
Saccharine	0.12
Flavoring	0.85
Water	Balance

The alumina abrasive had been prepared by rapidly heating gibbsite to between 500° C. and 800° C. at a rate of about 80° C. per minute and then continuing the heating until the temperature reached 1000° C. and maintaining the sample at 1000° C. until the total heating time was about two hours. The dentin abrasion value was 587 and the cleaning grade was 8.6. This abrasive is represented as point 19 of FIGURE 2. An analysis by X-ray diffraction showed 38% of the alumina to be kappa-type alumina. The balance of the alumina was amorphous.

Another toothpaste containing the same abrasive was made having the following composition:

	Percent
Abrasive	40.0
Sodium carboxymethyl cellulose	0.9
Glycerine	10.0
Sorbitol	20.0
Sudsing agents	1.9
Magnesium aluminum silicate	1.2
Saccharine	0.12
Flavoring	0.85
Water	Balance

A satisfactory toothpaste can also be made from the same formulation in which the abrasive is the alumina listed as sample No. 15 in Table III. This alumina contained 47% kappa-type alumina, 4% alpha alumina, less than 5% gamma alumina, and the balance substantially amorphous alumina.

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

If the alumina of this invention is to be incorporated in a tooth powder, the following range of formulations will provide satisfactory products.

Tooth powder formulations

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

An example of a very satisfactory tooth powder containing an alumina abrasive is as follows:

	Percent
Abrasive	96.0
Sudsing agent	3.0
Flavoring	0.6
Saccharine	0.4

The abrasive was prepared by heating gibbsite to a temperature of 500° C. at a rate of 80° C. per minute. The heating was continued until the temperature reached 1000° C., and the sample was held at this temperature for 65 minutes. The alumina had a median particle size of 5.5μ. The dentin abrasion value was 474 and the cleaning grade was 7.4. (This is shown as sample 20 of FIGURE 2.) Upon analysis, the sample was found to contain 55% kappa-type alumina and 45% amorphous alumina. No gamma or alpha alumina was present.

The dentifrices, both in paste and in powder form, may include additional materials which will provide desirable properties. Examples of such additional materials include, but are not limited to, sarcosinates, fluorine-containing compounds, quaternary ammonia compounds, chlorophyll, sodium dehydroacetates, sodium lauryl sulfate, tyrothrycin, penicillin, and hexacholorophene.

The method for measuring the amount of alumina phases present and for determining the polishing values, dentin abrasion values, and cleaning grades of abrasives are as follows:

MEASUREMENT OF ALUMINA PHASES

A determination of the composition of alumina can be made by measuring the relative intensities of the diffraction lines using a Geiger counter powder diffractometer. This is a parafocusing X-ray diffraction device which utilizes a Geiger counter for directly measuring the intensity diffracted at any particular angle 2θ. A complete description of this device may be found in "X-ray Diffraction Procedures," Klug and Alexander, published by John Wiley & Sons, Inc., New York City, 1954, beginning at page 235. By means of this device, the intensity diffracted at the various 2θ values can be shown as a line graph.

The procedure which can be used for measuring the relative amounts of various phases of alumina present in a sample can be adapted from the one set forth by Klug and Alexander (op. cit.) beginning at page 422. In this procedure, an internal standard is combined in varying proportions with samples of alumina, each of which is prepared so as to be substantially entirely in a single crystalline phase.

Crystalline samples of gamma, kappa, and alpha alumina are used in this procedure. Alumina substantially entirely in the gamma phase is prepared by slowly heating gibbsite to a temperature of 800° C. in such a manner that the temperature increases at a rate of less than 20° C. per minute, and then maintaining it at that temperature for at least 24 hours. FIGURE 1*b* is a diffraction pattern for such an alumina. Substantially pure kappa-phase alumina, shown in FIGURE 1*c*, is prepared by a similar slow heating of gibbsite to a temperature of 1000° C., and maintaining it at that temperature for 24 hours. Substantially pure alpha alumina, FIGURE 1*d*, is prepared by a similar slow heating of gibbsite to a temperature of 1250° C. and maintaining it at that temperature for 24 hours. The ratios of the intensities of selected diffraction lines of the alumina and of the internal standard for each of the combinations of the internal standard and a single phase alumina will provide data to produce a calibration curve for determining the relative amount of any single phase of alumina present in a mixture containing several phases.

Magnesium hydroxide has proved to be a satisfactory internal standard for use in quantitative determination of the phases of alumina in a sample, and the diffraction line at a spacing of 4.80 A. (18.5° 2θ) produced by the magnesium hydroxide is selected for measuring the intensity ratios.

The amount of alpha-phase alumina present in a sample is determined, using the diffraction line intensity at a spacing of 3.48 A. (25.6° 2θ). The amount of kappa-phase alumina present is then determined, using the diffraction line intensity at a spacing of 2.12 A. (42.6° 2θ).

To determine the amount of theta-phase alumina, the diffraction line intensity at a spacing of 2.73 A. (32.8° 2θ) is measured. Since kappa-phase alumina also has a weak line at the spacing of 2.73 A., the intensity measurement must be corrected for the kappa-phase contribution. The sum of the kappa-phase and theta-phase aluminas constitutes the amount of kappa-type alumina.

The amount of gamma-phase alumina present is determined by measuring the diffraction line intensity at a spacing of 1.39 A. (67° 2θ). Since both kappa-phase alumina and theta-phase alumina also contribute to this line, the measurement must be corrected for the contribution of these phases, and the amount of gamma-phase alumina can be determined.

When the total relative amounts of gamma, kappa, and alpha alumina present have been determined, any remaining alumina will be classed as "amorphous."

POLISHING

The enamel surface of a tooth is ground against glass, using a harsh abrasive, until a dull matte finish comparable to the dullest teeth observed in the mouth is produced on the surface of the tooth. The tooth is then brushed 5000 strokes with a slurry of the abrasive to be tested. A series of five standard teeth are used whose surface finishes range from a dull matte finish, assigned a value of 0, to the highest possible polish, having a value of 4. The polishing value of the abrasive to be tested is determined by visual comparison of the polished tooth with the standard teeth.

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 Wood's 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 radioactivity 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 IV.

TABLE IV

Particle diameter (μ):	Weight 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 the same concentration.

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 dicalcium orthophosphate dihydrate removes an average of 37.8 micrograms, multiplying this weight by the conversion factor (6.0) will give an abrasion value for the dicalcium phosphate dihydrate of 227.

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 V.

TABLE V

Particle diameter (μ):	Weight 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 VI.

TABLE VI

Particle diameter (μ):	Weight 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 infra-red 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 Du Pont 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 infra-red 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 3. 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 dentrifice 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 3 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 3. A straight line is drawn through these two points. By following the brushing and calculating procedure hereinbefore set forth, a sample abrasive is found to have a cleaning rating of 320. Referring to the line of FIGURE 3, 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.

As can be seen by the foregoing specification, the alumina particles of this invention are superior in polishing power to any of the commonly used dental abrasives. In addition, these alumina abrasives have equal or greater cleaning to dentin abrasive ratios when compared to conventional dental abrasives.

Having thus described my invention, what is claimed is:

1. The method of making an alumina dental abrasive material which comprises the steps of dehydrating gibbsite by heating it to a temperature within the range of from about 500° to about 800° C. at a rate of from 20° to 210° C. per minute, further heating the alumina thereby formed to a temperature within a phase conversion temperature range of from about 900° to about 1050° C., and maintaining the alumina at a temperature within the said phase conversion temperature range for more than one hour and until said alumina comprises from 20% to 55% kappa-type alumina, not more than 20% gamma-phase alumina, and not more than 10% alpha-phase alumina, the balance being substantially amorphous alumina.

2. A dental abrasive comprising particles of alumina, from 20% to 55% of said alumina being kappa-type alumina, not more than 20% of said alumina being gamma-phase alumina, not more than 10% of said alumina being alpha-phase alumina, and the balance being substantially amorphous alumina, said abrasive having a dentin abrasion value of not more than 700 and a cleaning grade of at least 7, substantially none of said particles having diameters greater than 20 microns.

3. A dentifrice comprising a sudsing agent and an abrasive, said abrasive comprising particles of alumina, from 20% to 90% of said alumina being kappa-type alumina, not more than 20% of said alumina being gamma-phase alumina, not more than 10% of said alumina being alpha-phase alumina, and the balance being substantially amorphous alumina, said abrasive having a dentin abrasion value of not more than 700 and a cleaning grade of at least 4, substantially none of said particles having diameters greater than 20 microns.

4. A dentifrice comprising a sudsing agent and an abrasive, said abrasive comprising particles of alumina, from 20% to 55% of said alumina being kappa-type alumina, not more than 20% of said alumina being gamma-phase alumina, not more than 10% of said alumina being alpha-phase alumina, and the balance being substantially amorphous alumina, said abrasive having a dentin abrasion value of not more than 700 and a cleaning grade of at least 7, substantially none of said particles having diameters greater than 20 microns.

References Cited in the file of this patent

UNITED STATES PATENTS

1,926,744	James	Sept. 12, 1933
2,000,857	Masin	May 7, 1935
2,010,910	Atkins	Aug. 13, 1935
2,550,207	Tainter	Apr. 24, 1951
2,750,258	Jukkola et al.	June 12, 1956
2,809,170	Cornelius et al.	Oct. 8, 1957

OTHER REFERENCES

Industrial and Engineering Chemistry, vol. 42, July 1950, pp. 1398–1403.

UNITED STATES PATENT OFFICE

CERTIFICATION OF CORRECTION

Patent No. 3,003,919 October 10, 1961

Robert W. Broge

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 2, line 18, for "innvention" read -- invention -- line 22, for "The diffraction pattern for gibbsite (alpha alumina" read -- The identifying terminology for the crystall forms --.

Signed and sealed this 3rd day of April 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents