3,378,445
PROPHYLACTIC DENTAL PASTE COMPOSITIONS COMPRISING ZIRCONIUM SILICATE AND TIN DIOXIDE

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No Drawing. Continuation-in-part of application Ser. No. 374,257, June 11, 1964. This application June 17, 1966, Ser. No. 558,270

The portion of the term of the patent subsequent to June 21, 1983, has been disclaimed 17 Claims. (Cl. 167-93)

This is a continuation-in-part of applicant's co-pend- 15 ing United States patent applications entitled Cleaning and Polishing Agent for Dental Prophylaxis, Ser. No. 374,-257, filed June 11, 1964, and Prophylactic Dental Paste Compositions Comprising Zirconium Silicate, now U.S. Patent No. 3,257,282.

The present invention relates to a new composition for cleaning and polishing teeth by dental prophylaxis and more specifically to a dental prophylaxis composition comprising a mixture of zirconium silicate (ZrSiO₄) and tin dioxide (SnO₂). While SnO₂ has various chemical names [e.g., "tin dioxide," "stannic oxide," "tin (IV) oxide," and "tin oxide"], for consistency, the name "tin dioxide" is used throughout this application.

Dental plaque, food particles, exogenous stains, and other tooth surface pigmentation can be removed, to varying degrees, from teeth by means of a suitable dentifrice and toothbrush, as in ordinary daily brushings. Some enamel stains and pigmentation, however, are much too resistant to the abrasives found in conventional dentifrice formulations. As a result, dentists must perform a "prophylaxis" in order to remove not only dental calculus (tartar) but the accumulated stains not satisfactorily removed by the daily use of a dentifrice. Most frequently, when either a dentifrice or the common cleaning and polishing agents used to perform a prophylaxis are employed, the teeth may be cleaned, but they exhibit a low luster or polish. For good dental esthetics, clean teeth with a high luster are desired, and it would be desirable to provide a cleaning and polishing agent capable of accomplishing these results.

The problems encountered in the relatively infrequent use of a cleaning and polishing agent in a prophylactic paste, for example, a prophylaxis performed once or twice a year, are much different than the problems encountered in the use of a cleaning and polishing agent as a con- 50 stituent of a dentifrice for use two or three times a day, even though the desired end result of cleaning and polishing of enamel may be the same. Obviously, it is possible to use a more highly abrasive agent in a prophylactic paste than in a daily brushing with a conventional dentifrice. However, care must be taken in both cases to avoid excessive oral hard tissue loss at the expense of cleaning action. In general, it has been assumed that in attempting to remove the more difficult forms of stain (e.g., tobacco, green, stannous flouride, silver nitrate, etc.) there must be a major compromise between cleaning and tooth structure loss, or, in other words, that, in order to have maximum removal of these more difficult stains and/or pigmentations, tooth structure must be sacrificed. It would be desirable to provide a cleaning and polishing composition for dental prophylaxis which effectively removes even the most difficult enamel stains and pigmentation while minimizing hard tooth structure loss due to abrasion.

Another factor which should be considered in the development of a suitable prophylaxis is the ability to polish 70 the teeth to a high luster, that is, to achieve smooth and

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highly lustrous enamel surfaces. Highly polished surfaces apparently are less receptive to retention of plaque and oral debris, and this factor is one of the motivating reasons for developing a cleaning and polishing agent which not only cleans effectively but which produces an exceptionally good luster. However, good luster heretofore could not be achieved without sacrificing cleaning or increasing abrasiveness.

Little, if any, relationship appears to exist either between the cleaning and the polishing abilities of dental abrasives or between the abrasiveness and the ability of the abrasive to produce a smooth tooth surface. For example, levigated alumina is an excellent polishing agent which produces a very smooth and shiny surface, but it is so abrasive that resultant tooth structure loss precludes its recomendation for use. Precipitated chalk, on the other hand, cleans fairly well but produces a rough tooth surface. Dicalcium phosphate is relatively unabrasive, but it fails to effectively polish. A mixture of insoluble sodium metaphosphate and tricalcium phosphate is a fairly effective polishing agent, but the combination is not a particularly good cleaning agent. The most common agent used in current day dental prophylaxis is flour of pumice. This agent is a fair cleaner, but it is highly abrasive and produces an exteremely poor polish. In fact, recent studies have shown that the resulting tooth surface is so rough after being treated with flour of pumice that the occurrence of dental calculus, stains, pellicle, and other oral debris is significantly increased.

Thus, it would be highly desirable to provide an effective cleaning and polishing agent which minimizes oral hard tissue damage. As has been indicated, a variety of compounds are known which clean well but which do not polish, or which polish well but do not clean satisfactorily. The aforesaid Ser. No. 374,257 application discloses that zirconium silicate having a particular particle size distribution may be employed as a dental prophylaxis cleaning and polishing agent capable of achieving the desired cleaning and polishing performance. In particular, the said application describes a zironium silicate composition having particles distributed in three different levels, namely, a first level of up to about 20 microns particle size, a second level of from about 20 up to about 50 microns, and a third level of from about 50 up to about 70 microns. In 45 preferred practice, the said levels are combined in a composition having percentage ratio ranges of about 10-50% in the first level, 5-25% in the third level, and the balance in the second level. The smaller particles of the first level are provided primarily to carry out a polishing function and in order to remove pellicle from oral hard tissues (i.e., enamel, dentin, and cementum); the particles of the second level are provided in order to clean and to remove stain; and the particles of the third level are provided for cleaning non-organic restorative materials (e.g., metal fillings, amalgams, inlays, and the like) and for removing severe stains [e.g., green stain and stannous fluoride (SnF2) pigmentation].

In accordance with the present invention, it has been found that a new and even more effective dental prophylax-60 is cleaning and polishing agent may be obtained by admixing zirconium silicate with tin dioxide. Preferably, such an agent comprises at least about 50 and up to about 99% zirconium silicate and the balance tin dioxide. An especially preferred agent comprises a 9:1 weight ratio mixture of zirconium silicate and tin dioxide. Preferably, the zirconium silicate particles are distributed throughout three levels substantially in accordance with the percentage ratio ranges set forth in the aforesaid Ser. No. 374,257 application. The tin dioxide particles substantially all fall within the range of up to about 3 microns and preferably of up to about 2 microns. An especially effective compo-

sition is obtained by employing zirconium silicate containing substantially no particles of less than about 10 microns particle size.

The compositions of the present invention are capable of polishing oral hard tissue even better than the compositions of the said Ser. No. 374,257 application. This result may be achieved without any diminution in the cleaning capabilities of the composition. Another advantage of the zirconium silicate-tin dioxide cleaning and polishing compositions of the present invention is that when they 10are employed in carrying out dental prophylaxis treatments, dental handpiece wear is reduced relative to certain other cleaning and polishing compositions. Moreover, the compositions of the present invention, when provided in paste form, are easier to use and handle than certain 15 other cleaning and polishing compositions.

The aforesaid U.S. Patent No. 3,257,282 describes prophylactic paste compositions comprising zirconium silicate as a cleaning and polishing agent and a fluoride-containing anticariogenic adjuvant. The said application teach- 20 es that the utilization of zirconium silicate as a cleaning and polishing agent in a dental prophylaxis composition markedly enhances the effectiveness of anticariogenic adjuvants contained in such compositions. It has been found, and forms a further aspect of the present invention, that 25 the zirconium silicate-tin dioxide compositions of the present invention likewise enhance the effectiveness of anticariogenic adjuvants contained in a therapeutic prophylactic paste composition and in some instances are even superior to compositions containing zirconium silicate 30 alone.

It is, therefore, a primary object of the present invention to provide a new and improved dental prophylaxis composition comprising an admixture of zirconium silicate and tin dioxide.

A related object of the present invention is to provide a dental prophylaxis composition comprising zirconium silicate and tin dioxide of defined particle size ranges and distributions.

Yet another object is to provide an agent for dental pro- 40 phylaxis that effectively removes the most difficult enamel stains and pigmentations while minimizing loss of oral hard tissue.

A further object of this invention is to provide a dental prophylaxis agent adapted to polish all accessible tooth surfaces to a high luster while effectively cleaning such

A still further object is to provide a dental prophylaxis agent adapted for cleaning and polishing oral hard tissues in order to render them less receptive to the reten- 50 tion of dental calculus, plaque, and other oral debris such

Another object is to provide a dental prophylaxis composition suitable for admixture with a fluoride-containing anticariogenic adjuvant in order to produce a thera- 55 peutic (i.e., anticariogenic) dental prophylaxis mixture.

Yet another object is to provide a dental prophylaxis composition which is easier to handle and use in comparison with prior art prophylactic compositions, and which in use does not produce objectionable dental handpiece wear.

A further object is to provide new dental prophylaxis methods adapted to clean and polish teeth effectively and, in addition, to reduce the incidence and severity of dental caries.

These and other objects, advantages, and features of the present invention will hereinafter appear, and, for purposes of illustration, but not of limitation, exemplary embodiments of the present invention are hereinafter described in detail.

Formulation, characteristics, and manner of use

In accordance with the present invention, it has been found that mixtures of zirconium silicate and tin dioxide

use in dental prophylaxis. It has also been found that when an effective amount of a fluoride-containing anticariogenic adjuvant is admixed with such a zirconium silicate-tin dioxide mixture, a superior therapeutic (i.e., anticariogenic) prophylaxis composition is obtained.

The size of particles in a cleaning and polishing composition can be expressed in a number of different ways, one of the most common of which is "mean diameter," i.e., the diameter above which one-half of the particles are larger and below which one-half are smaller. As hereinafter utilized, the term "particle size" refers to a mean diameter value.

The dental cleaning and polishing agents of the present invention preferably comprise at least about 50% and up to about 99% ZrSiO₄ and balance SnO₂ (i.e., a 99:1-1:1 ZrSiO₄-SnO₂ weight ratio range). An optimal preferred range is at least about 75% and up to about 92.5% ZrSiO₄ and balance SnO₂ (i.e., a 12.33:1–3:1 ZrSiO₄–SnO₂ weight ratio range). The preferred agent of the present invention comprises 90% ZrSiO₄ and 10% SnO₂ (i.e., a 9:1 weight mixture of ZrSiO₄ and SnO₂).

The zirconium silicate particles are preferably distributed over three defined levels, namely, a first level of up to about 20 microns particle size; a second level of from about 20 microns up to about 50 microns particle size; and a third level of from about 50 up to about 75 microns particle size. Preferably, the said levels are combined in a composition having percentage ratio ranges of about 10-50% in the first level; 5-25% in the third level; and the balance in the second level. Substantially all of the tin dioxide particles are of less than about 3 microns particle size and preferably substantially all are less than about 2 microns particle size. When zirconium silicate and tin dioxide having particles distributed in accordance with the described ranges and distributions are admixed, a superior cleaning and polishing prophylaxis agent is obtained.

In its generic sense, the zirconium silicate that is mixed with tin dioxide differs from that set forth and described in the aforesaid Ser. No. 374,257 application only in that the upper level for zirconium silicate particles is about 75 microns rather than 70 microns as disclosed in the aforesaid application, it having been found that the presence of a minor amount of particles lying in the 70-75 micron range produces no undesirable side effects when combined with the specified amount of tin dioxide, that is, the loss in polishing effectiveness that would be expected to result from the presence of a zirconium silicate having particle sizes above 70 microns is more than compensated for by the increase in polishing capability attributable to the presence of tin dioxide in the composition of the present invention.

The zirconium silicate component of the composition of the present invention is distributed throughout the said three levels in order to accomplish the several different functions a satisfactory prophylaxis composition must be capable of performing. Thus, the particles of the first level (i.e., the smallest particles) are provided primarily to carry out a polishing function and in order to remove pellicle from oral hard tissues; the particles of the second level are provided in order to clean and to remove stain; and the particles of the third level (i.e., the largest particles) are provided for cleaning non-organic restorative materials and for removing severe stain. As 65 mentioned above, the tin dioxide particles are provided primarily in order to enhance the polishing capability of the over-all composition.

An especially preferred zirconium silicate agent adapted for admixture with tin dioxide comprises particles dis-70 tributed in the range of about 10-75 microns, that is, substantially no particles of less than about 10 microns particle size are included in the agent. Thus, a preferred zirconium silicate formulation finds the zirconium silicate particles being distributed in a first level of from exhibit optimal cleaning and polishing characteristics for 75 about 10 up to about 20 microns; second level of from

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about 20 up to about 50 microns; and a third level of from about 50 up to about 75 microns, the percentage ratio range for the zirconium silicate particles being about 10-50% in the first level; 5-25% in the third level; and balance in the second level. While it is preferable that no zirconium silicate particles of less than about 10 microns particle size be provided in the mixture, nonetheless, because of practical difficulties of obtaining a mixture that is completely free of under 10 microns particles, acceptable tolerances permit up to about 1% zir-conium silicate particles of less than about 10 microns in such a preferred composition.

Especially preferred zirconium silicate mixtures adapted to be mixed with tin dioxide comprise zirconium silicate distributed in accordance with the values given in 15 Table I. This zirconium silicate is admixed with an appropriate amount of tin dioxide of less than about 3 microns and preferably less than about 2 microns particle

TABLE I

		Per	cent
	Particle Size	Acceptable Percentage Ranges	Preferred Distribution
Level I (22-28%)	{>0μ; <10μ >10μ; <20μ	<1.00 22-27	0.0 24.7
Level II (balance)	$\begin{array}{l} >20\mu; <30\mu_{} \\ >30\mu; <40\mu_{} \\ >40\mu; <50\mu_{} \end{array}$	20-24 17-22 12-15	$\frac{22.3}{19.5}$
Level III (16-22.1%)	>50μ; <60μ >60μ; <70μ	6-8 3-4	13. 7 7. 3 3. 8
	>70μ; <75μ >75μ;	< 0.1	8.7 0.0
			100.0

The preparation of suitable particle size zirconium silicate and tin dioxide may be accomplished by conventional milling and segregation techniques. Basically, these techniques involve milling of zirconium silicate and tin dioxide ores, followed by standard screen sieving to segregate the desired particle size (e.g., a standard 400 mesh screen retains approximately 95% of 35± 3% micron particle size). The exact mode of preparation and segregation of particle sizes forms no part of the subject invention and substantially any acceptable preparation techniques may be employed so long as the desired particle size ranges and distributions are obtained.

The zirconium silicate-tin dioxide prophylaxis compositions of the present invention may be applied in the oral cavity in an aqueous slurry form as a part of a conventional prophylaxis, although in some instances (e.g., in the treatment of silver amalgams and of gold inlays) 50the composition may be introduced directly to the area of treatment. In general, a minimum amount of water (e.g., 15 parts per 100 parts cleaning and polishing composition) should be utilized for maximum cleaning, and cleaning and polishing composition) should be utilized for maximum polishing. Of course, each treatment should be handled on an individual basis, depending upon the exigencies of the circumstances.

It should also be understood that various other materials (such as flavoring agents) may be added to the zirconium silicate-tin dioxide cleaning and polishing composition described herein, so long as such composition is employed as the essential cleaning and polishing medium in the prophylaxis treatment.

A particularly useful mode of application of the zirconium silicate-tin dioxide cleaning and polishing composition of the present invention is in the form of a paste. Such a paste may be packed and distributed in any suitposition be packaged in collapsible tubes. A prophylaxis may be more easily and efficiently performed using a paste packaged in tube form.

A prophylactic paste composition would conventionally

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cleaning and polishing composition) other conventional agents such as flavoring materials (e.g., oil of wintergreen, oil of peppermint, oil of spearmint, oil of sassafras, oil of anise, and the like); sweetening agents (e.g., saccharin, dextrose, levulose, sodium cyclamate, and the like); binders (e.g., water-soluble salts of cellulose ethers such as sodium carboxymethyl cellulose and sodium carboxymethyl hydroxyethyl cellulose); natural gums (e.g., gum karaya, gum arabic, and gum tragacanth) as thickeners; humectants (e.g., glycols, glycerin, sorbitol, and other polyhydric alcohols); and coloring agents.

The composition of a typical prophylaxis paste and a method of formulation therefor are given in the following Example.

Example I

Lample 1	
Ingredient: Amount (percent by	weight)
ZrSiO ₄	66.99
SnO_2	7.44
Distilled water	7.44
Glycerin (USP)	6.89
70% Aqueous sorbitol solution (USP)	9.49
Sodium carboxymethyl hydroxyethyl	2
cellulose	1.30
Sweeteners	0.04
Coloring agent	0.13
Flavoring agent	0.28
	100.00

The distilled water is placed in a stainless steel mixing dish, and the sweetener (e.g., saccharin) is first dissolved in the water and thereafter the sorbitol, coloring agent, and flavoring agent are added and thoroughly mixed. Tin dioxide is slowly added to the mixture and mixed well until all lumps are dispersed. Thereafter, zirconium silicate is added and is also mixed until the paste has a smooth consistency. The glycerin is measured and placed in a separate container and the sodium carboxymethyl hydroxyethyl cellulose is added thereto and mixed in order to form a binder composition. The binder composition is slowly added to the zirconium silicate-tin dioxide-containing mixture and the resulting combination is stirred until the binder is well dispersed throughout the paste mixture and has undergone hydration. The paste is then deaerated and may be tubed in a conventional manner.

Manner of use

A typical method of application for a prophylactic dental paste composition produced in accordance with the present invention is given in the following example.

Example II

The following procedure is preferred for thorough cleansing and polishing of the teeth on an annual or semiannual basis as required. Each tooth is thoroughly scaled more fluid mixtures (e.g., 25 parts water per 100 parts 55 in order to remove all calculus and soft debris. After scaling is completed, the buccal-labial surfaces of the maxillary right quadrant are polished using a soft rubber cup and an excess of prophylactic paste (which may either be squeezed from a tube as needed or which may be formulated by the dentist or dental hygienist as desired). Each surface of the tooth is treated for at least ten seconds. Then the lingual surfaces of the maxillary right quadrant are correspondingly treated. Unwaxed dental floss (which may be supplied in kit form with the prophylaxis paste) is used in all interproximals and preferably is utilized with an excess of the prophylactic paste. The patient may be allowed to rinse thoroughly with water any time during the treatment.

After rinsing, the lingual one-half of the maxillary able container, but it is preferred that such a paste com- 70 left quadrant is polished and the patient is allowed to rinse. The bucco-labial one-half of the maxillary left quadrant is polished, but the patient is not allowed to rinse until all of the interproximal contacts have been cleaned and polished with the unwaxed dental floss. The embody (in addition to a zirconium silicate-tin dioxide 75 buccal and lingual surfaces of the mandibular right

molars and bicuspids are than polished. Unwaxed dental floss is used in the interproximals before rinsing.

The mandibular anterior teeth are polished next, both labillary and lingually, and the interproximal areas are polished with the unwaxed dental floss before rinsing is allowed. The buccal and lingual surfaces of the mandibular left molars and bicuspids are then polished, the interproximals are dental flossed, and the patient is allowed to rinse. The occlusal surfaces and all pits and fissures are then polished with a stiff bristle prophylactic brush 10 are also reported in Table ii.

the brushing so that the loss of weight attributable to the prophylaxis can be measured.

The dentin loss caused by the zirconium silicate-tin dioxide composition of the present invention and by various commercially available prophylaxis compositions were determined in accordance with the previously described method for both human and bovine dentin. These values are reported in Table II. Human and bovine enamel loss data were obtained in a similar manner and

TABLE II.—SUMMARY OF ENAMEL AND DENTIN ABRASION DATA OBTAINED WITH VARIOUS PROPHYLACTIC PASTE COMPOSITIONS

	Enamel A	brasion	Dentin Al	orasion
Cleaning and Polishing Composition	Human Enamel (mg.)	Bovine Enamel (mg.)	Human Dentin (mg.)	Bovine Dentin (mg.)
Zirconium silicate, tin oxide	27. 06±4. 25 26. 56±3. 26 41. 55±5. 58 49. 41±7. 54 50. 70±8. 50 34. 58±3. 84 23. 74±2. 82 22. 78±3. 54 24. 69±4. 62 29. 56±3. 24 28. 37±2. 29 49. 28±8. 37 30. 74±4. 20 49. 28±8. 37 49. 49±5. 60	27. 60±5. 65 23. 10±3. 65 48. 18±6. 03 40. 21±7. 92 41. 23±6. 37 39. 56±6. 89 26. 85±5. 32 29. 86±7. 56 26. 71±7. 42 40. 51±5. 43 41. 23±9. 80 44. 68±5. 21 28. 12±5. 21 28. 12±5. 68	134. 6±13. 3 169. 4±20. 6 222. 6±17. 8 245. 4±18. 4 150. 4±19. 1 127. 2±11. 4 138. 0±14. 0 151. 3±10. 5 175. 8±32. 1 179. 2±19. 7 161. 5±20. 3 163. 9±13. 5 121. 0±13. 9 166. 7±14. 4	186±19. 178. 4±15. 249. 4±19. 278. 2±14. 294. 2±27. 272. 2±17. 143. 0±24. 144. 2±29. 100. 4±12. 159. 9±27. 155. 8±14. 229. 1±14. 240. 0±32. 233. 9±21. 162. 9±22. 268. 8±30.

*A zirconium silicate composition in accordance with the teachings of the aforesaid Serial No. 374,257 application accordance with the teachings of the aforesaid Serial No. 374,257 application accordance with the teachings of the aforesaid Serial No. 374,257 application accordance with the teachings of the aforesaid Serial No. 374,257 application accordance with the teachings of the aforesaid Serial No. 374,257 application accordance with the teachings of the aforesaid Serial No. 374,257 application accordance with the teachings of the aforesaid Serial No. 374,257 application accordance with the teachings of the aforesaid Serial No. 374,257 application accordance with the teaching serial No. 374,257 application acco

and the prophylactic paste. The patient is then allowed to 30 rinse his mouth as thoroughly as possible.

Enamel and dentin abrasion properties

Zirconium silicate is a well-known industrial abrasive which is used for grinding and polishing glass and ceram- 35 ics. The extreme hardness and abrasion characteristics exhibited by zirconium silicate (e.g., a hardness number of 7.5 on the Mohs' scale for commercially available zirconium silicate of type used for grinding of glass) would suggest to one skilled in the art that zirconium silicate 40 would seriously damage (i.e., abrade and scratch) oral hard tissues and would thus be unsuitable for use as a constituent in a dental prophylaxis cleaning and polishing composition. However, experimental evaluations of the zirconium silicate-tin dioxide compositions of the present invention have revealed that such compositions may in fact be safely employed without removing substantial amounts of oral hard tissue. Tooth dentin is frequently found exposed at the surface of the teeth near the free gingival margin, particularly in clinical cases where the gingiva have receded. The abrasion of tooth dentin by a prophylaxis agent is much greater than the abrasion of tooth enamel by the same agent, i.e., 10-100 times. Consequently, the dentin abrasion is considered to be of greater importance than the enamel abrasion, and the effect of a cleaning and polishing agent on dentin is used as an important criterion in the selection of suitable agents. The zirconium silicate-tin dioxide mixture utilized in accordance with the subject invention has a highly satisfactory dentin abrasion characteristic, a fact which is quite surprising in view of the innate hardness of the zirconium silicate constituent thereof.

The method for determining dentin abrasion values for dental cleaning and polishing agents is as follows. The dentin portions are separated from human central incisors, and each dentin portion is mounted in a low melting alloy, such as Wood's metal, and is submerged in a slurry of the cleaning and polishing agent to be tested in a 3% carboxymethyl cellulose solution. An automatic toothbrush is arranged so that it can be moved back and forth across the surface of the submerged portion of the dentin, and the pressure of this toothbrush is adjusted to 150 grams. The tooth dentin is subjected to the brushing action for 50,000 double strokes, and removed from the slurry. The dentin portion is weighed before and after 75 experimental prophylaxis paste or agent, the enamel sur-

The data of Table II verify that the compositions of the present invention may be safely employed in carrying out dental prophylaxis treatments.

Enamel polishing properties

The enamel polishing properties of the zirconium silicate-tin dioxide prophylaxis compositions of the present invention have been compared with various commercially available dental prophylaxis agents and pastes. The polishing agents and pastes were evaluated in accordance with the so-called "prophylaxis cup polishing procedure." In accordance with this method, the lingual surfaces of freshly extracted maxillary anterior teeth are reduced with the aid of a diamond disc, and the teeth are mounted by means of a low melting alloy, such as Wood's metal, on hexagonal jigs constructed so as to fit the movable stage of a reflectometer. The exposed labial surface of each tooth is mounted in such a manner that the height of the contour is a suitable distance above the base of the jig. Throughout the procedure, care is taken to ensure that the teeth do not become dry in order to prevent damage of the tooth tissues. The exposed enamel surface is then dulled by exposing it to 0.10 percent hydrochloric acid (pH 2.2) for 30 seconds. Any acid remaining on the tooth surface is neutralized by immediately transferring the tooth to a saturated sodium carbonate solution for 30 seconds. The tooth is then rinsed with water and blotted

The maximum reflectance of the dulled tooth surface is determined by means of a reflectometer especially 60 adapted to detect the changes in the degree of polish of the enamel surface. The reflectometer is constructed so that the enamel is exposed to a beam of polarized light, and the amount of light reflected from the enamel surface is determined by a photoelectric cell which in turn activates a galvanometer. The smoother the enamel surface, the smaller the amount of diffused and absorbed light and, hence, the higher the galvanometer reading.

After the maximum reflectance of the dulled tooth is determined, the tooth is polished through the use of a dental engine, conventional handpiece, and a rubber prophylaxis cup, the speed of the engine being held constant at 5000 r.p.m. The handpiece is permanently mounted so as to ensure equalized pressure. After the tooth has been polished for exactly 30 seconds with a slurry of the

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face is rinsed with water so as to remove any residual particles of the cleaning and polishing agent, and the reflectance of the enamel surface is again measured with the tooth located in exactly the same position as that used to obtain the "dull" reading. The change in the amount of reflectance between the dulled and the polished enamel surface is taken as a measure of the degree of polish imparted by the prophylaxis treatment.

In order to express all measurements in terms of a recognized standard polishing agent, each series of tests includes a treatment of the teeth with a specific sample of dry calcium carbonate (#300; Wittaker, Clark, & Daniels Co.) as a reference standard, and all data are expressed relative to this agent in terms of a polishing ratio.

Polishing ratios obtained for the composition of the present invention and for the various commercially available agents and pastes are given in Table III, which also contains a percent superiority figure for the compositions of the present invention.

TABLE III.—COMPARATIVE POLISHING PROPERTIES OF VARIOUS DENTAL PROPHYLAXIS AGENTS AND PASTES

Cleaning and Polishing Agent	Polishing Ratio	Polishing Superiority (Percent Superiority)	25
Zirconium silicate, tin dioxide	22.79		•
Zirconium silicate *	18.58	22.7	
Quartz-pumice	13.63	67.2	
Pumice-mire	16.23	40. 4	
Pumice-feldspar	15.21	49.8	
Kaonnite-quartz	15.88	43. 5	30
Aragonite-calcite (paste)	10.56	115.8	50
Aragonite-calcite (tablet)	13.37	70. 5	
Calcite	14.81	53.9	
Calcite-pumice	12.56	81.4	
Quartz-calcite	8, 59	165.3	
Anatase-pumice-quartz-feldspar	8.44	170.0	
Quartz-talc-montmorillonite	8.30	174.6	
Montmorillonite-quartz	2.67	753.6	35
Al(OH)3-pumice	10.56	115.8	30
Quartz-feldspar	7 74	104.4	

 $^{^{*}\,\}mathrm{A}$ zirconium silicate composition in accordance with the teachings of the aforesaid Ser. No. 374,257 application.

Metal polishing properties

In addition to being an excellent agent for polishing oral hard tissues, the zirconium silicate-tin dioxide compositions of the present invention exhibit superior polishing capabilities when employed to polish dental restorative materials, such as silver amalgam and gold, as verified by the following experimental evaluation.

Gold and amalgam restorations were polished in the previously described manner, with the maximum reflectance being determined before and after the polishing treatment. Determinations were made for: (1) a zirconium silicate-tin dioxide agent produced in accordance with the present invention; (2) a zirconium silicate composition produced in accordance with the teachings of the aforesaid Ser. No. 374,257 application; and (3) a mixture of zirconium silicate plus 10% stannous silicate (Sn₂SiO₄). The increase in reflectance (in absolute reflectometer units) obtained with these agents for gold and silver amalgam is given in Table IV. The data of Table IV verifies the high level of polishing effectiveness of the compositions of the present invention for use on restorative materials.

TABLE IV.—POLISHING OF METAL RESTORATIONS

Cleaning and Polishing Composition	Net Increase in Polishing Units		
	Amalgam	Gold	
(1) ZrSiO ₄ +10% SnO ₂ (2) ZrSiO ₄ (3) ZrSiO ₄ +10% Sn ₂ SiO ₄	2,00 1,15 1,15	4.95 4.60 3.20	

Cleaning and polishing properties of various ZrSiO₄-SnO₂ mixtures

The cleaning capability of a prophylaxis paste composition may be experimentally evaluated by means of a cleaning grade test. This test, the procedure of which is 75

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more fully set forth and described in Cooley et al. U.S. Patent No. 3,151,027, involves the use of polyester plastic blocks specifically designed for use in an electric tooth-brushing machine. The blocks are ground smooth, washed, and dried, and a thin coat of black lacquer is carefully applied to the surface of the block. The blocks are then inserted in the toothbrushing machine and brushed with various cleaning and polishing compositions for a set number of strokes at a constant pressure. Reflectance measurements of the blocks are obtained with a reflectometer, all measurements being expressed relative to a calcium pyrophosphate standard. The results are expressed as cleaning scores on a scale of from 0 to 6.5, a higher value indicating a greater cleaning ability.

Polishing ratios (relative to a CaCO₃ standard) and cleaning scores obtained in the foregoing manner for various zirconium silicate-tin dioxide mixtures are given in Table V. These mixtures range from a 100% zirconium silicate composition to a 100% tin dioxide composition.

TABLE V.—SUMMARY OF CLEANING AND POLISHING DATA PERTINENT TO RATIO OF $ZrSiO_4$ TO SnO_2

Cleaning	and Polishin	~		
ZrSiO ₄ -SnO ₂ Ratio	Percent by Weight		 Polishing Ratio 	Cleaning Score
Itatio	ZrSiO ₄	SnO_2	-	
1:0	100.0	0.0	18.58	5, 53
99:1	99.0	1.0	21, 27	5. 56
97. 5:2. 5	97.5	2, 5	21.48	5, 53
19:1	95.0	5, 0	21.48	5.56
92.5:7.5	92.5	7.5	23.97	5, 60
9:1	90.0	10.0	23. 31	5.63
17:3	85.0	15.0	23, 43	5.55
4:1	80.0	20.0	23. 02	5, 60
3:1	75. 0	25.0	23, 22	5, 53
1:1	50.0	50.0	22.85	5.53
1:3	25.0	75.0	22.10	3.40
0:1	0.0	100.0	21. 15	2.13

The data of Table V verify that superior cleaning and polishing results are obtained with the zirconium silicatetin dioxide mixture comprising at least about 50% and up to about 99% ZrSiO₄ and balance SnO₂ (i.e., a 99:1–1:1 ZrSiO₄-SnO₂ weight ratio range). An optimal preferred range is at least about 75% and up to about 92.5% ZrSiO₄ and balance SnO₂ (i.e., a 12.33:1–3:1 ZrSiO₄-SnO₂ weight ratio range). The preferred mixture of the present invention comprises 90% ZrSiO₄ and 10% SnO₂ (i.e., a 9:1 weight mixture of ZrSiO₄ and SnO₂).

Dental handpiece wear

An especial advantage of the improved cleaning and polishing compositions of the present invention is that the dental handpieces used in performing prophylaxis treatments is minimized, as shown by the following experimental evaluation.

Handpiece wear measurements throughout a series of three prophylaxis treatments were obtained for four different prophylaxis compositions. Before the first treatment and at the end of each successive treatment, the (1) loss in shoulder diameter of the prophy angle; (2) loss in diameter of the angle lip; (3) loss in diameter inside screw; (4) loss in weight of screw cap; and (5) loss in weight of shaft and gear were measured. The four prophylactic compositions evaluated were: (1) a zirconium silicate 65 cleaning and polishing agent produced in accordance with the teachings of the aforesaid Ser. No. 374,257 application; (2) a zirconium silicate composition produced in accordance with the said Ser. No. 374,257 application, but having substantially no particles of less than 10 microns 70 particle size; (3) a 9:1 weight ratio of composition (1) and tin dioxide; and (4) a 9:1 weight ratio of composition (2) and tin dioxide. The latter two compositions fall within the generic scope of the subject invention, with composition (4) being a preferred composition. The data obtained in this manner are reported in Table VI.

TABLE VI.-SUMMARY OF DATA CONCERNING EFFECT OF VARIOUS PROPHYLACTIC PASTES UPON THE WEAR OF PROPHY ANGLES

THIS WINDOWS THE								
Cleaning and Polishing Composition	Treatment No.	Loss in Diameter at Shoulder (in.)	Loss in Diameter at Lip (in.)	Loss in Diameter Inside Screw (in.)	Loss in Weight of Screw Cap (mg.)	Loss in Weight of Shaft and Gear (mg.)		
Composition (1) ZrSiO ₄	1st 2nd 3rd	0. 0005 0. 0020 0. 0020	0. 0035 0. 0005 0. 0000	0. 0005 0. 0005 0. 0005	5. 3 1. 5 3. 2	7. 2 5. 7 7. 6		
Total		0.0045	0.0040	0.0015	10.0	20. 5		
Composition (2) ZrSiO ₄ >10μ	1st 2nd 3rd	0. 0010 0. 0010 0. 0005	0. 0020 0. 0010 0. 0005	0. 0010 0. 0010 0. 0020	5. 4 5. 7 2, 9	2, 5 3, 3 5, 2		
Total		0.0025	0. 0035	0.0040	14.0	11.0		
Composition (3) 9:1 ZrSiO ₄ -SnO ₂₋	1st 2nd 3rd		0. 0010 0. 0020 0. 0010	0. 0005 0. 0000 0. 0000	2. 0 1. 6 3. 4	1. 7 3. 6 5. 3		
Total		0.0015	0.0040	0. 0005	7. 0	10.6		
Composition (4) 9:1 ZrSiO ₄ -SnO ₂ (ZrSiO ₄ $>$ 10 μ).	1st 2nd 3rd	0.0010	0. 0030 0. 0000 0. 0000	0. 0005 0. 0010 0. 0010	3. 6 0. 8 0. 5	3. 0 1. 1 0. 3		
Total		0. 0020	0.0030	0. 0025	4. 9	4.4		

The data of Table VI demonstrate that the compositions of the present invention, and particularly the preferred composition of the present invention may be employed without excessive dental handpiece wear. Moreover, this attribute is achieved without any loss in cleaning and polishing effectiveness.

Therapeutic prophylactic pastes

As previously indicated, the zirconium silicate-tin dioxide cleaning and polishing agent of the present invention also functions as a compatible carrier for anticariogenic adjuvants in therapeutic (i.e., anticariogenic) prophylactic paste compositions. Preferably, the adjuvant should be presented in the form of fluoride-containing compounds capable of supplying fluoride and stannous ions or combinations thereof, for example, with an additional component, such as zirconium ions or germanium ions, in biologically available form.

The preferred adjuvants are stannous fluorozirconate (SnZrF₆), stannous fluoride (SnF₂), and complex zirconium-germanium fluorides [e.g., Zr(GeF6)2, ZrOGeF6, Ge(ZrF₆)₂, ZrGeF₈, ZrGeF₆, and ZrOGe₄]. Stannous fluorozirconate and the indicated complex salts appear to be the best anticariogenic fluoride-containing adjuvants now known to the dentifrice arts, especially by virtue of the absence of objectionable taste, lack of enamel pigmentation, freedom from damaging gingival tissue, and increased anticariogenic effectiveness obtainable therewith.

Other suitable adjuvants include water-soluble fluoride salts such as NaF, SnF4, KF, InF3, PdF2, FeF2, and LiF, as well as more complex water-soluble fluoride-containing adjuvants such as fluorosilicates, e.g., Na₂SiF₆, other fluorozirconates, e.g., CaZrF₆, Na₂ZrF₆, and K₂ZrF₆, fluorostannites, e.g., NaSnF₃, fluoroborates, e.g., NaBF₄, fluorotitanates, e.g., NaTiF₅, other fluorogermanates, e.g., K₂GeF₆, and mixed halides, e.g., SnClF and Sn₂ClF₃. Mixtures of suitable adjuvants may also be utilized. Another suitable adjuvant comprises a mixture of a fluoride salt 60 was formulated in a conventional manner: and an active phosphate compound as set forth and described in applicant's co-pending United States patent application, Anticariogenic Comopositions and Methods, Ser. No. 535,022, filed Mar. 17, 1966.

In general terms, where the foregoing essential ingredi- 65 ents are used in formulating a therapeutic prophylactic paste composition, fluoride ion is employed at an effective and non-toxic level, usually within a range of from about 1 to about 15%, by weight of the composition. When SnF₂ or SnZrF₆ are utilized, such salts are preferably 70 This prophylactic base may be formulated into a theraemployed at a level of about 8% and 30%, respectively (i.e., about 8% SnF2 supplies about 3% fluoride ion and about 30% SnZrF6 supplies about 10% fluoride ion). The compatible zirconium silicate-tin dioxide cleaning and polishing mixture is employed within a range of from 75 about 4% fluoride ion) content to the resulting prophylac-

about 30% to 80%, by weight of the prophylactic paste composition.

Therapeutic prophylactic paste compositions may be prepared in a conventional manner and usually include additional ingredients that render the over-all composition commercially acceptable. For example, as previously indicated, prophylactic paste compositions typically embody conventional components such as bleaching agents, binders, humectants, flavoring agents, and the like.

A specific example of a therapeutic prophylactic paste produced in accordance with the present invention is 35 given in the following example.

Example III

	Constituent:	Percent by weight	ght
	ZrSiO ₄		63
_			~
U	SnZrF ₆		20
	Liquide		10

Such a therapeutic prophylactic paste may conveniently be formulated and prepared for distribution and use in tube form in accordance with the general method of Example I, above.

However, in many instances, because of the loss of anticariogenic effectiveness attributable to the tendency of stannous ion-containing materials to oxidize and hydrolyze over time in an aqueous environment, it may be desirable to formulate the prophylactic paste just prior to application. This may be accomplished by adding the fluoride-containing anticariogenic adjuvant at the last minute to a prophylactic base containing the zirconium silicate, tin dioxide and other prophylactic paste constituents. The following example is illustrative of this manner of practicing the subject invention.

Example IV

A prophylactic base having the following constituents

Constituent: Percent by w	
ZrSiO ₄	69.3
SnO ₂	
Bleaching agents (e.g., TiO ₂)	4.0
Binders (e.g., sodium carboxymethyl hydroxy-	
ethyl cellulose)	0.22
Humectants (e.g., glycerin)	
Sweetening and flavoring agents	1.0

peutic prophylactic paste by dissolving 0.3 gram of stannous fluoride in 1 milliliter of distilled water and by adding the aqueous solution thereby formed to 2.0 grams of the foregoing base, giving approximately a 9% SnF₂ (i.e.,

tic paste. As an alternative, 0.93 gram of SnZrF6 may be dissolved in 1.0 cc. of distilled water, and the aqueous solution can be added to 2.0 grams of the foregoing prophylactic base, giving approximately a 24% SnZrF₆ (i.e., about 9% fluoride ion) content to the resultant prophylactic paste.

Experimental evaluations of zirconium silicate-tin dioxide prophylactic paste formulations as described herein indicate that the zirconium silicate-tin dioxide mixtures function as effective fluoride and stannous ion compatible carrier vehicles. In order to assess the effectiveness of a material as a compatible carrier vehicle for anticariogenic adjuvants, one analytical technique that is conventionally employed is a so-called "percentage availability" determination.

Percentage availability refers to a comparison of an ionic concentration level for a combination of carrier vehicle and of adjuvant relative to the corresponding ionic concentration level for a reference solution of the adjuvant without the carrier vehicle (e.g., an aqueous solution 20 of the adjuvant maintained at a reference ionic concentration level, such as 1000 p.p.m. fluoride). A percentage ratio of the ionic concentration level for the combination solution relative to the reference solution is expressed as a percentage availability (e.g., a combination solution of carrier vehicle and stannous fluoride which analyzes 900 p.p.m. fluoride concentration compared to a reference solution of stannous fluoride at 1000 p.p.m. fluoride exhibits a 90% availability insofar as ability to provide aqueous fluoride ions is concerned).

Table VII gives exemplary percentage availability data for fluoride and, in some instances, stannous ions for various fluoride systems, i.e., (1) sodium fluoride (NaF) at 1000 p.p.m. fluoride ion; (2) NaF at 1000 p.p.m. fluoride plus 10% monosodium dihydrogen phosphate 35 (NaH₂PO₄); (3) stannous fluoride (SnF₂) at 1000 p.p.m. fluoride ion; (4) SnF₂ at 1000 p.p.m. fluoride ion plus $10\%\ NaH_2PO_4;$ (5) $8\%\ SnF_2;$ and (6) $8\%\ SnF_2$ plus 8%NaH₂PO₄, and for several cleaning and polishing compositions, i.e., (1) a zirconium silicate cleaning and pol- 40 ishing composition obtained in accordance with the teachings of the aforesaid Ser. No. 374,257 application; (2) composition (1), but with all zirconium silicate particles of less than 10 microns removed; (3) a 4:1 weight mixture of zirconium silicate and tin dioxide (i.e., a 20% 45 SnO₂ composition); (4) a 9:1 zirconium silicate-tin dioxide mixture (i.e., 10% SnO₂); and (5) a 19:1 weight mixture of zirconium silicate and tin dioxide (i.e., a 5% SnO₂ mixture).

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The same essential prophylaxis treatment procedure may be employed whether a therapeutic (i.e., anticariogenic) or a non-therapeutic prophylaxis composition is used. In addition to the excellent cleaning and polishing results obtained with a non-therapeutic zirconium silicate-tin dioxide-containing composition, the provision of a fluoridecontaining anticariogenic adjuvant in the composition permits the added benefit of the anticariogenic attributes of fluoride-containing compounds for reducing the incidence and limiting the severity of dental caries to be

As indicated by the foregoing data, the invention disclosed herein, in one of its aspects, provides a method for reducing the solubility of the oral hard tissue comprising the application thereto of a prophylactic paste composition formulated from a zirconium silicate-tin dioxide cleaning and polishing agent together with an effective amount of a fluoride-containing anticariogenic adjuvant. In addition, the present invention includes a new and improved method for cleaning and polishing the teeth comprising the application thereto of a prophylaxis composition comprising zirconium silicate and tin dioxide.

While therapeutic and non-therapeutic prophylaxis compositions of the present invention are typically employed in a professional prophylaxis (i.e., a prophylaxis performed in a dental office by a dentist or dental hygienist), the present invention also encompasses use of 30 such pastes on a non-professional self-administered home

While the subject invention has been described with reference to certain exemplary embodiments, it should be understood that various changes, modifications, and alterations may be effected in the materials utilized, in the proportions of materials, and in the manners of formulating the compositions, without departing from the spirit and the scope of the subject invention, as defined in the appended claims.

What is claimed is:

1. A dental prophylaxis composition for cleaning and polishing teeth comprising as a cleaning and polishing component a mixture of uncoated zirconium silicate, ZrSiO₄, and uncoated tin dioxide, SnO₂, wherein the zirconium silicate, ZrSiO4, has a distribution of mean diameter particle sizes in the range of up to about 75 microns and the tin dioxide, SnO2, has a distribution of mean diameter particle sizes in the range of up to about

TABLE VII.—SUMMARY OF PERCENTAGE AVAILABILITY DATA

	*	Percent Availability with Various Abrasive Systems									
Fluoride System	Concentration	Composition (1) ZrSiO ₄		Composition (2) ZrSiO ₄ >10μ		Composition (3) 4:1 ZrSiO ₄ -SnO ₂		Composition (4) 9:1 ZrSiO ₄ -SnO ₂		Composition 19:1 ZrSiO ₄ -Sn	
		Tin. Percent	Fluoride, Percent	Tin, Percent	Fluoride, Percent	Tin, Percent	Fluoride, Percent	Tin, Percent	Fluoride, Percent	Tin, Percent	Fluoride, Percent
NaF NaF	1,000 p.p.m. F 1,000 p.p.m. F	,	94.89		98.63		94.30		98.82		97. 25
plus NaH2PO4	10%	}	85.75	-+	96.88		95.10		96.00		98.89
nF ₂	1,000 p.p.m. F 1,000 p.p.m. F	93.63	83.74	94. 33	93.09	72.62	77. 23	79.59	81.71	82.15	86.26
plus NaH•PO•	10%	59.68	46. 19	87.56	85.21	41.53	75.45	86.36	88.03	83.94	89.93
nF ₂	8%	98.53	91.92	89.82	98.56	95.06	100.00	100.00	98.56	90, 82	97.12
plus IaH2PO4	8%	85.88	77. 33	88.52	84.11	85.65	87.51	88.97	87.51	103. 10	86, 38

The data of Table VII demonstrate that the zirconium exhibit a high level of stannous and fluoride ion compatibility which is in many instances higher than corresponding values obtained with compositions comprising zirconium silicate alone as their cleaning and polishing components.

- 3 microns and wherein the zirconium silicate, ZrSiO₄, is silicate-tin dioxide compositions of the present invention 70 provided in said mixture at a level of at least about 50 and up to about 99%, by weight of said mixture, the balance of said mixture being tin dioxide, SnO2.
 - 2. A composition, as claimed in claim 1, wherein said mixture comprises at least about 75 and up to about 75 92.5% zirconium silicate, ZrSiO₄.

- 3. A composition, as claimed in claim 1, wherein said mixture comprises about 90% zirconium silicate, ZrSiO4, and about 10% tin dioxide, SnO2.
- 4. A composition, as claimed in claim 1, wherein the zirconium silicate, ZrSiO4, has a distribution of mean diameter particle sizes in a first level of up to about 20 microns, in a second level of from about 20 microns up to about 50 microns, and in a third level of from about 50 microns up to about 75 microns, the three levels being combined in a percentage ratio range of about 10-50% 10 of the first level, 5-25% of the third level, and the balance of the second level, and wherein the tin dioxide, SnO₂, has a distribution of mean diameter particle sizes in the range of up to about 3 microns.

5. A composition, as claimed in claim 4, wherein the 15 tin dioxide, SnO2, has a distribution of mean diameter particle sizes in the range of up to about 2 microns.

6. A composition, as claimed in claim 4, wherein the zirconium silicate, ZrSiO4, has a distribution of mean diameter particle sizes with the following ranges:

	ercentage range
>0;<10>10;<20	22–27
>20;<30 >30;<40	20–24 25
>40;<50	10 15
>50;<60	6-8
>60;<70	
>75	

7. A composition, as claimed in claim 6, wherein the zirconium silicate, ZrSiO4, particle size distribution con- 35 forms to the following values:

Particle size range (μ) :	Percent
>0;<10	0.0
>10:<20	24.7
>20:<30	22.3
>30:<40	19.5
>40;<50	13./
>50;<60	7.3
>60;<70	3.8
>70;<75	
>75	0.0

- 8. A therapeutic prophylactic paste composition comprising an anticariogenically effective and non-toxic amount of at least one fluoride-containing anticariogenic adjuvant and as a cleaning and polishing component a mixture of uncoated zirconium silicate, ZrSiO4, and uncoated tin dioxide, SnO2, wherein the zirconium silicate, ZrSiO₄, has a distribution of mean diameter particle sizes in the range of up to about 75 microns and the tin dioxide, SnO₂, has a distribution of mean diameter particle sizes in the range of up to about 3 microns, wherein the zirconium silicate, ZrSiO4, is provided in said mixture at a level of at least about 50 and up to about 99%, by weight of said mixture, the balance of said mixture being tin dioxide, SnO2, and wherein said mixture is provided in the over-all composition at a level of about 30-80%, by weight of the over-all composition.
- 9. A composition, as claimed in claim 8, wherein the fluoride-containing anticariogenic adjuvant is provided in the over-all composition at a level of from about 1-15%, by weight of the over-all composition, calculated as fluoride ion.
- 10. A composition, as claimed in claim 9, wherein said mixture comprises at least about 75 and up to about 92.5% zirconium silicate, ZrSiO₄.
- 11. A composition, as claimed in claim 9, wherein the zirconium silicate, ZrSiO₄, has a distribution of mean di- 75 the over-all composition at a level of from about 1-15%,

- ameter particle sizes in a first level of up to about 20 microns, in a second level of from 20 microns up to about 50 microns, and in a third level of from about 50 microns up to about 75 microns, the said three levels being combined in a percentage ratio range of about 10-50% of the first level, 5-25% of the third level, and balance of the second level, the tin dioxide, SnO2, having mean diameter particle sizes in the range of up to about 3 microns.
- 12. A composition, as claimed in claim 11, wherein the tin dioxide, SnO₂, has a distribution of mean diameter particle sizes in the range of up to about 2 microns.
- 13. A composition, as claimed in claim 11, wherein the zirconium silicate, ZrSiO4, has a distribution of mean diameter particle sizes within the following ranges:

>10;<20 >20;<30 >30;<40 >40;<50	>1.00 22-27 20-24 17-22 12-15 6-8	
>20;<30	20-24	
>30:<40	1/-22	•
>40:<50	12–15	•
		i
>60:<70	3_4	
	7–10)
	<0.1	

14. A composition, as claimed in claim 13, wherein the zirconium silicate, ZrSiO4, particle size distribution conforms to the following values:

Particle size (µ):	Preferred distribution percent
\0:_10	0.0
>10:/20	24.7
> 20, < 20	22.3
>20,<30	19.5
>30;<40	13.7
>40;<50	13.7 7.3
>75	0.0

- 15. A method for cleaning and polishing teeth comprising the application thereto of a dental prophylaxis composition comprising as a cleaning and polishing com-45 ponent a mixture of uncoated zirconium silicate, ZrSiO₄, and uncoated tin dioxide, SnO₂, wherein the zirconium silicate, ZrSiO4, has a distribution of mean diameter particle sizes in the range of up to about 75 microns and the tin oxide, SnO2, has a distribution of mean diameter particle sizes in the range of up to about 3 microns and wherein the zirconium silicate, ZrSiO4, is provided in said mixture at a level of at least about 50 and up to about 99% by weight of said mixture, the balance of said mixture being tin dioxide, SnO₂.
 - 16. A method for cleaning and polishing teeth and reducing the incidence of dental caries therein comprising the application thereto of a dental prophylaxis composition comprising an anticariogenically effective and non-toxic amount of at least one fluoride-containing anticariogenic adjuvant and as a cleaning and polishing component a mixture of uncoated zirconium silicate, ZrSiO4, and uncoated tin dioxide, SnO₂, wherein the zirconium silicate, ZrSiO4, has a distribution of mean diameter particle sizes in the range of up to about 75 microns and the tin dioxide, SnO2, has a distribution of mean diameter particle sizes in the range of up to about 3 microns, wherein the zirconium silicate, ZrSiO₄, is provided in said mixture at a level of at least about 50 and up to about 99%, by weight of the mixture, the balance of said mixture being tin dioxide, SnO2, and wherein said mixture is provided in the over-all composition at a level of about 30-80%, by weight of the over-all composition.
 - 17. A method, as claimed in claim 16, wherein the fluoride-containing anticariogenic adjuvant is provided in

3,378,445

17	18
by weight of the over-all composition, calculated as fluo- ride ion.	3,151,027 9/1964 Cooley et al 167—93 3,257,282 6/1966 Muhler 167—93
References Cited UNITED STATES PATENTS	3,257,282 6/1966 Muhler 167—93 FOREIGN PATENTS
1,529,486 3/1925 Kaemmerling et al 167—93 2,427,799 9/1947 Maloney 151—308	5 462,610 1/1950 Canada. 180,531 1/1936 Switzerland.
2,941,926 6/1960 Salzmann et al 167—93 3,105,013 9/1963 Saul et al 167—93	RICHARD L. HUFF, Primary Examiner. LEWIS GOTTS, Examiner.