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(54) **Multi-component dentifrice comprising rehydrated silica gel**

(57) A dentifrice containing a rehydrated silica gel abrasive cleansing agent, the rehydrated silica gel constituting 5 to 80% by weight of the dentifrice, having an average particle size of 5 to 18 μm, containing at least 25% by weight of water and being prepared by drying a silica hydrogel to a water content of about 20% by weight or less and rehydrating the gel to at least 25% by weight of water.

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SPECIFICATION

Multi-component dentifrices

This invention is concerned with multi-component dentifrices containing an improved silica abrasive.

Modern dentifrice compositions contain numerous components that have various therapeutic and cosmetic functions. Most of these compositions contain an abrasive cleansing agent which aids in the removal of adherent deposits on the teeth. Particulate matter of specific hardness and certain particle size, shape and structure are utilized as such abrasives. These particles must also be compatible with other toothpaste ingredients and safe for repeated human use. Abrasives that are described in the patent literature and have found commercial application include silica xerogels, hydrated silicas, hydrated aluminas, calcium carbonate, dicalcium phosphate (anhydrous and dihydrate), calcium pyrophosphate, and insoluble sodium metaphosphate. These agents are usually 2 to 30 micrometers (μm) in size. Products of about 10 μm appear to find the most commercial acceptance. Insoluble crystalline materials such as quartz have been found too abrasive for safe use on human teeth.

The use of silica xerogels is described in U.S. Patent No. 3,538,230 to Pader & Weisner. This patent teaches that hydrogels prepared by acidifying a sodium silicate solution and then dried to a water content of 0.6 to 6% provide a xerogel that can be used as an abrasive especially for translucent and transparent toothpastes. U.S. Patent No. 4,153,680 to Seybert teaches the use of a hydrogel as an abrasive for a dentifrice. This patent discloses that hydrogels prepared by neutralizing a sodium silicate solution and dried to between 17 and 32% water are effective abrasives. An important teaching of this patent is that the gel cannot be dried significantly below the level desired and then rehydrated to produce an effective product.

We have found that hydrated silica prepared by dehydrating a hydrogel with subsequent rehydration provides excellent abrasive action when formulated in dentifrice compositions.

According to the present invention therefore a multi-component dentifrice is provided containing a rehydrated silica gel abrasive cleansing agent, the rehydrated silica gel constituting 5 to 80% by weight of the dentifrice, having an average particle size of 5 to 18 μm, containing at least 25% by weight of water and being prepared by drying a silica hydrogel to a water content of about 20% by weight or less and rehydrating the gel to at least 25% by weight of water.

The rehydrated silica gel preferably contains at least about 30%, more preferably 25% to 45% and even more preferably 33% to 42%, by weight of water.

The silica hydrogen is preferably dried to a water content of about 15%, more preferably from 5% to 20% and even more preferably 5% to 15%, by weight.

The silica may be prepared for example by forming a hydrogen from a soluble silicate and acid, dehydrating the hydrogen and then rehydrating the silica. Our rehydrated silica is easily combined with other dentifrice components and provides the desired cleansing abrasiveness.

The rehydrated silica that we have found useful as an abrasive for dentifrices may be prepared for example as follows. A hydrogel containing 60% to 75% water is prepared by neutralizing a soluble silicate solution. In general, mineral acids such as H_2SO_4 or HNO_3, are the neutralizing agents; however, acid-reacting salts and other materials are also useful. The neutralizing agent is mixed with the silicate solutions, and the mixture is allowed to gel. The solid gel is crushed before washing to remove the salts formed during neutralization and any other undesirable soluble impurities. The washed gel may be milled to the desired particle size before drying, or the milling may be subsequent to the drying. In any case, any convenient method of drying can be employed using temperatures of 40 to 500°C, preferably 50 to 350°C. The washed or dried gel can be milled in most mills capable of reducing the particle size of the gel to about 10 μm average particle size with a range of particles of 0.5 to 40 μm. The dried gel contains between 5 and 20% water. This gel is then treated with water to rehydrate the material. This treatment can be carried out in any convenient manner that does not result in hard agglomerates. The resulting free-flowing white powder is readily incorporated into dentifrice compositions to provide the desired cleansing abrasiveness.

We prefer to prepare rehydrated silica by the following method. A sodium silicate solution containing about 25% SiO_2 is mixed with sufficient H_2SO_4 at about 45% to produce a hydrosol at about 18% SiO_2 and with an excess of acid over that needed to completely neutralize the sodium in the silicate. The silicate and acid are combined using a mixing device wherein no localized concentration deformities are realized. We prefer to use a mixing nozzle as the mixing device. The hydrosol sets to a hydrogel which is crushed to a convenient size for washing. The crushed hydrogel is washed with water, adjusted to 3.5 pH with H_2SO_4 until a slurry of the gel has the desired final pH, such as, for example, 3.7 to 5.1. The gel now contains about 28% SO_2. The washed gel can be milled or dried as the next step. We prefer to use a fluid energy mill or an air swept hammer mill to reduce the particle size to 5 to 18 μm. While any convenient drying method can be used to reduce the water content from more than 65% to between 5 and 15%, we prefer that at least one portion or segment of the drying step be carried out at 150 to 350°C. Then water is added to the silica gel, usually in a device that agitates the material as the water is added and equilibrated. The final product is a fine white powder that contains 25 to 45% water and has a particle size of 5 to 18 μm. We prefer a product that contains 33 to 42% water. We determine water content by the loss on ignition (LOI), heating the sample to 1300°C.

Surprisingly, our rehydrated silica gels are more effective abrasives than hydrogels or xerogels, as determined in radioactive dentin abrasion tests. We tested a series of four hydrogels that had an average of about 31% water content. We tested a series of

eleven xerogels which had an average water content of 9.86%. Both series of gels exhibited an average of 25.4 RDA units per gram of anhydrous silica. We also tested a series of nine rehydrated silica gels with an average water content of about 32%. Our material exhibited an average of 29.8 RDA units per gram of anhydrous silica. Calcium pyrophosphate was used as a standard of comparison for the RDA tests, and it was considered to have a value of 10.0 RDA units per gram of $Ca_2P_2O_7$.

Sufficient rehydrated silica can be used in dentifrice compositions to provide the required cleansing abrasion. In general, about 15 to 25% silica abrasive is inclined in a dentifrice. Since the rehydrated material has superior abrasive qualities, as little as 5% silica can be used. A dentifrice may contain as much as 80% silica abrasive. We prefer to use 10 to 65% of our rehydrated silica as the abrasive.

Numerous other ingredients constitute the balance of the dentifrice and provide various therapeutic, cosmetic and conditioning functions. Compounds containing stannous or calcium ions are added as therapeutic agents. Fluorine compounds are also reputed to provide various benefits. Stannous fluoride is often used in various toothpastes. Humectants prevent hardness in the toothpaste and include, among others, glycerol, sorbitol and propylene glycol. Binders are important for the obvious reason, and include gum tragacanth, sodium carboxymethylcellulose, methylcellulose, hydroxyethylcellulose, propylene glycol alginates, Indian gum, Irish moss, carrageenan starch, agar agar and the like. Other ingredients include soaps and synthetic detergents, flavouring agents such as sweeteners, and oxygen releasers, buffers, preservatives and coloring agents.

The radioactive dentin abrasion (RDA) test indicates the abrasive properties of various materials and is carried out as follows. Eight radioactive teeth (neutron activation) are brushed 1000 times with various abrasives formulated into a standard paste. This standard paste consists of 6.25 g of the silica abrasive or 10.0 g of calcium pyrophosphate suspended in 50 ml of 0.5% carboxymethylcellulose in water. The entire thick slurry is used in the test brushing. These proportions translate into a silica content of about 12%, which is slightly below current commercial practice for toothpastes utilizing silica abrasives. The quantity of abraded tooth material is determined from the slurry, which contains radioactive material after the brushing. The results are compared to the calcium pyrophosphate standard which is assigned an RDA value of 100. Missouri Analytical Laboratories in St. Louis performed these tests for us. Hydrogels and xerogels as well as the rehydrated silicas of our invention were tested in this manner and the results are summarized in the following table.

Table I

Radioactive Dentin Abrasion Values for Silicas

Silica Abrasive	*LOI (%)*	*RDA (units)*	*RDA (value corrected anhydrous SiO_2)*	*RDA (RDA/g SiO_2)*
hydrogel	29.4	102	119	23.3
hydrogel	34.7	95	145	23.3
hydrogel	42.3	87	151	24.1
xerogel	6.7	132	141	22.6
xerogel	8.3	120	131	20.9
xerogel	7.8	139	151	24.1
xerogel	5.4	169	183	28.6
rehydrated	32.0	145	213	33.3
rehydrated	29.8	146	208	33.3
rehydrated	42.8	128	224	35.8
rehydrated	27.2	133	188	30.0

These results indicate clearly that rehydrated silica is a more effective abrasive than the hydrogel or xerogel. Rehydration of a dried silica gel must induce a structural change in the silica since the results for the hydrogels and xerogels are about equivalent, while the rehydrated materials have improved performance.

The following Example in which all proportions are in parts by weight (pbw) or weight percent (%) unless otherwise specified, illustrates certain embodiments of our invention.

Example

An initial hydrogel was prepared as follows. A commercially available sodium silicate solution was diluted so that it contained 25.4% SiO_2 and 7.89% Na_2O. A sulfuric acid solution was prepared to contain 45.6% H_2SO_4. These two solutions were mixed using a mixing nozzle so that the formation of localized gel was avoided. The flow rates were 3,000 cc/minute for the silicate and 1020 cc/minute for the acid. The temperature of the resulting sol was 51°C. The sol contained 18.9% SiO_2 and had a gel time of about 5 minutes. This gel was backwashed with deionized water adjusted to 3.5 pH until it had a slurry pH of 4.2. The washed gel had a SiO_2 content of 28.04% and a LOI of 71.95%. This material was milled to about 10 μm in a fluid energy mill.

A sample of the initial hydrogel prepared as described above was dried for a short period of time at 150°C to 9.6% water content, thereby forming a xerogel. This material was incorporated into a toothpaste and a RDA value of 110 (25 RDA/g of SiO_2)

was obtained.

A second sample of the initial hydrogel was dried slowly at less than 100°C to 7% water. The RDA value of this xerogel was 120 (20.6 RDA/g SiO_2).

A third sample was dried to about 10% at 150°C, then sufficient water to bring the LOI up to 32.0% was added and allowed to equilibrate while maintaining the gel in motion, providing a rehydrated silica. The RDA value was 145 (34.1 RDA/g SiO_2).

Still another sample of the initial hydrogel was partially dried at 105°C. The remainder of the water to 9.5% was removed at 310°C. This material was rehydrated to 34.0% water in the same manner as the previous sample. The RDA value was 122 (29.6 RDA/g SiO_2).

These results indicate that the rehydrated silicas are more efficient as toothpaste abrasives than xerogels.

CLAIMS

1. A multi-component dentifrice containing a rehydrated silica gel abrasive cleansing agent, the rehydrated silica gel constituting 5 to 80% by weight of the dentifrice, having an average particle size of 5 to 18 μm, containing at least 25% by weight of water and being prepared by drying a silica hydrogel to a water content of about 20% by weight or less and rehydrating the gel to at least 25% by weight of water.

2. A dentifrice as claimed in claim 1 wherein the rehydrated gel contains at least about 30% by weight of water.

3. A dentifrice as claimed in claim 1 wherein the rehydrated gel contains 25% to 45% by weight of water.

4. A dentifrice as claimed in claim 3 wherein the rehydrated gel contains 33% to 42% by weight of water.

5. A dentifrice as claimed in claim 1, 2, 3 or 4 wherein the silica hydrogel is dried to a water content of from 5% to 20% by weight.

6. A dentifrice as claimed in claim 5 wherein the silica hydrogel is dried to a water content of from 5% to 15% by weight.

7. A dentifrice according to any of claims 1 to 6 wherein the rehydrated silica gel constitutes 10 to 65% by weight of the dentifrice.

8. A dentifrice as claimed in any of claims 1 to 7 wherein the silica hydrogel is dried at a temperature of 40°C. to 500°C.

9. A dentifrice as claimed in claim 8 wherein the silica hydrogen is dried at a temperature of 50°C. to 350°C.

10. A dentifrice as claimed in any of claims 1 to 9 wherein at least one portion of the drying of the silica hydrogen is carried out at a temperature of 150°C. to 350°.

11. A dentifrice as claimed in any of claims 1 to 10 wherein the rehydrated gel is brought to a particle size of 5 to 18 μm by means of a fluid energy mill or an air swept hammer mill.

12. A dentifrice as claimed in any of the preceding claims wherein the silica hydrogel is obtained from a hydrogel made by mixing sodium silicate solution with sulphuric acid using a mixing nozzle.

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