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(54) **Fluoroaluminosilicate glass powder for dental glass ionomer cement**

(57) A fluoroaluminosilicate glass powder for dental glass ionomer cement, the surface of which is treated with a fluoride in an amount of from 0.01 to 5 parts by weight based on 100 parts by weight of the glass powder. The fluoroaluminosilicate glass powder of the invention not only has improved physical properties such as crushing strength but also improved mixing workability without impairing the inherent characteristics thereof for dental use.

**GB 2 180 833 A**

## SPECIFICATION

**Fluoroaluminosilicate glass powder for dental glass ionomer cement**

- 5 The present invention relates to a fluoroaluminosilicate glass powder for dental glass ionomer cement. 5
- Glass ionomer cement which is used mainly in dentistry is prepared by setting a fluoroaluminosilicate glass powder and a polycarboxylic acid such as polyacrylic acid in the presence of water, and a set body thereof has transparency and is aesthetically acceptable. Further, it has no irritant
- 10 action with respect to a dental pulp and has excellent biocompatibility. Still further, it exhibits an excellent adhesion to enamel and dentin tooth substances, has good marginal sealing, and exhibits durability in the mouth over a long period of time. Also, since the glass powder contains fluorine, it can be expected that it has a tooth substance-strengthening function. In view of these characteristics, the dental glass ionomer cement is widely used in various applications
- 15 such as restoration and filling of dental cavities, cementing of prostheses and orthodontic bands, lining of dental cavities, core construction, and as pit and fissure sealant. 15
- However, with respect to this glass ionomer cement, when a polyacrylic acid aqueous solution and a fluoroaluminosilicate glass powder are merely combined and mixed, the mixed material has low fluidity and poor workability. Further, it requires a long period of time for setting, and the
- 20 surface thereof is broken by contact with saliva, whereby not only does the surface of the cement become weak but also its final strength is not satisfactory. 20
- In order to overcome these defects, a number of methods have been investigated. For example, Japanese Laid-Open Patent No. 101893/1977 discloses a method by which the above-described defects are overcome and the characteristics of the glass ionomer cement are main-
- 25 tained by providing a setting liquid comprising a 45–60% aqueous solution of polyacrylic acid or an acrylic acid copolymer having incorporated therein from 7 to 25%, based on the total weight, of one or more polybasic carboxylic acids. Further, the present applicant has disclosed in Japanese Laid-Open Patent No. 2210/1982 a dental glass ionomer cement setting liquid comprising a 45–55% aqueous solution of an acrylic acid/maleic acid copolymer having incorporated
- 30 therein from 10 to 25% of tartaric acid and from 0.1 to 5% of at least one fluorocomplex salt, based on the total weight. Still further, various other attempts have been made. In accordance with these methods, not only the physical properties but also workability and water resistance are improved. 30
- While various improvements in the dental glass ionomer cement have been investigated, the
- 35 fluidity of the mixed paste is still insufficient as compared with that of a zinc phosphate cement which has hitherto been widely used and, therefore, it cannot yet be said that the workability is wholly satisfactory. In particular, when the glass ionomer cement is used for cementing of prostheses, the flow is so poor that the cement film is likely to thicken and, hence, the fitting of the prosthesis was often unsatisfactory. That is, at the time when the manipulation can be
- 40 performed immediately after the mixing, it is necessary to increase the fluidity of the cement without adversely affecting the physical properties. Further, when the glass ionomer cement is used for filling, since it has inferior physical properties such as crushing strength as compared with dental amalgams or dental composite resins, a glass ionomer cement of improved crushing strength is needed depending upon symptoms. 40
- In order to overcome the above-described disadvantages, the present inventors have made
- 45 extensive investigations regarding a glass powder which is used for dental glass ionomer cement and have surprisingly found that, when a surface of a fluoroaluminosilicate glass powder is treated with a fluoride in an amount of from 0.01 to 5 parts by weight based on 100 parts by weight of the glass powder, not only are its physical properties such as crushing strength
- 50 improved, but also the fluidity of a mixed cement is increased to improve the workability, and as a result the present invention has been accomplished. 50
- Accordingly, the present invention provides a fluoroaluminosilicate glass powder for dental glass ionomer cement, a surface of which is treated with a fluoride in an amount of from 0.01 to 5 parts by weight based on 100 parts by weight of the glass powder.
- 55 A dental glass ionomer cement using a fluoroaluminosilicate glass powder, the surface of which is treated with a fluoride, leads to increased fluidity of a cement paste immediately after mixing and improved manipulation for mixing. Therefore, when it is used for cementing of prostheses, there is an effect that the film of the cement does not become readily thick. Further, the time required for cement workability until the initial setting in which the fluidity of the cement
- 60 surface completely disappears is shortened, and the setting proceeds sharply. That is, it is possible to prolong the working time while the initial setting time remains the same. Still further, a dental glass ionomer cement using a glass powder treated with a fluoride has improved physical properties such as crushing strength. 60
- As the fluoroaluminosilicate glass powder used in the present invention, there can be used a
- 65 powder which is prepared by melting, as main components, silica ( $\text{SiO}_2$ ) and alumina ( $\text{Al}_2\text{O}_3$ ) 65

together with, as a melting agent, a fluoride or a phosphate at high temperatures of 1000°C or higher, followed by cooling and grinding. Any fluoroaluminosilicate glass powder which reacts with a polycarboxylic acid in the presence of water can be used in the present invention.

5 However, in general, those fluoroaluminosilicate glass powders which are prepared by melting a mixed component containing from 25 to 50% of silica, from 15 to 40% of alumina, from 10 to 40% of a fluoride, and from 0 to 20% of a phosphate at high temperatures of 1000°C or higher, followed by cooling and grinding, are preferably used. Further, with respect to the silica and alumina, it is only required that they are present in equivalent amounts as raw materials for glass, and any other materials which can be expected to have a similar function in the glass are employable. For example, it is possible to replace part or the whole of silica or alumina by aluminium silicate, silica gel, aluminium hydroxide, etc. if the equivalent amount is ensured. For example, if aluminium hydroxide is used as a raw material in place of alumina, there is an advantage that the melting can be readily performed. In this case, the proportion of the aluminium hydroxide as calculated in terms of the alumina content may be determined.

15 Examples of the fluoride which is used as one of the raw materials of glass include not only fluorides of zinc, aluminium, yttrium, lanthanum and zirconium, in addition to those of alkali metals and alkaline earth metals, but also fluorocomplex salts such as sodium hexafluoroaluminate ( $\text{Na}_3\text{AlF}_6$ ) and potassium hexafluoroaluminate ( $\text{K}_3\text{AlF}_6$ ).

20 Examples of the phosphate which is also used as one of the raw materials for glass include phosphates of alkali metals, alkaline earth metals, zinc, aluminium, yttrium, lanthanum and zirconium. The phosphate is not particularly restricted to an orthophosphate, but various other phosphates such as pyrophosphates, monobasic phosphates, and dibasic phosphates can be used.

The fluoroaluminosilicate glass powder can suitably contain, as raw materials, oxides, carbonates, and hydroxides. For example, oxides, carbonates, and hydroxides of alkaline earth metals, yttrium, lanthanum, zinc, zirconium and titanium, can be added as raw materials for use.

25 As the fluoroaluminosilicate glass powder prepared by melting and grinding the above-described raw materials, a powder which passes through a #80 sieve is preferred, and a powder which passes through a #150 sieve is particularly preferred. Further, in the case that the powder is particularly prepared for the use of cementing, the maximum diameter thereof is preferably 25  $\mu\text{m}$  or less.

30 The fluoride which is used for the surface treatment of the fluoroaluminosilicate glass powder is not particularly restricted, but in general metal fluorides are preferred. Examples of the metal fluoride which can be used include aluminium fluoride, zinc fluoride, tin fluoride, zirconium fluoride, acidic sodium fluoride, acidic potassium fluoride, and various fluorocomplex salts such as sodium hexafluoroaluminate ( $\text{Na}_3\text{AlF}_6$ ) or potassium hexafluoroaluminate ( $\text{K}_3\text{AlF}_6$ ). Among them, the fluorocomplex salts disclosed in Japanese Laid-Open Patent No. 2210/1982 by the present applicant are particularly preferred.

35 Of the fluoride and fluoroaluminosilicate glass powder are simply mixed and dispersed, neither the fluidity of the cement paste immediately after the mixing is increased nor is an improvement in workability achieved. Such effects are realized first by the treatment of the surface of the glass powder with a fluoride. It is quite important from the clinical standpoint that the fluidity is improved.

40 That is, first of all, the working time of the cement is increased without delay of the initial setting time. The glass ionomer cement is generally supplied in the form of a powder and liquid to clinicians. Depending upon the product, a liquid component may be powdered and then added to a powder component, followed by mixing with water. In any of the cases, when a dentist actually uses the cement, since the cement is used upon mixing, it is required that the cement has as much allowance as possible, whereas it rapidly sets as fast as possible at the stage when the working has been completed. Accordingly, the setting characteristic greatly influences the clinical practice. This setting characteristic is greatly improved by the surface treatment of the glass powder with a fluoride.

45 Secondly, since the fluidity of the mixed cement is increased, the mixing is readily performed, i.e. the mixing workability is improved. Thus, it can be expected to minimize differences obtained by individuals who perform the mixing.

50 Thirdly, in the case that the glass ionomer cement is used for cementing of prostheses or orthodontic bands, the cement layer thereof can be made thin. This means that in the case that the glass ionomer cement is present between a prosthesis and a tooth, not only is the adhesion of a prosthesis to a tooth substance improved, but also the durability can be improved.

55 Further, the above-described treatment increases the strength of a hardened cement. The increase in the strength can be effected by merely mixing the glass powder with the fluoride. However, the strength is further increased by the surface treatment. This is considered to be caused because, since a setting reaction of the cement is assumed to take place on the glass powder surface, its effect is larger in the surface-treated glass powder. The fluidity of the mixed cement can be specifically investigated by, for example, a consistency measurement method as described below. That is, the consistency measurement method is a method in which 0.5 ml of

the mixed cement paste is measured and placed on a glass plate, and one minute after the start of the mixing another glass plate is placed on the cement paste together with a load, to thereby measure the spread of the cement.

One example in which a difference in consistency between a cement powder added with the fluoride and a cement powder treated with the fluoride was specifically measured is given below.

A fluoroaluminosilicate glass powder prepared by melting a raw material containing 40% of silica sand, 26% of alumina, 20% of fluorite, 5% of aluminum fluoride, 2% of sodium fluoride, and 7% of calcium phosphate and then grinding the mixture was mixed with a glass ionomer cement setting liquid (Fuji Ionomer Type I, G-C Dental Industrial Corp.) in a ratio of powder to liquid of 1.5/1.0, and the consistency was found to be 22 mm. When to this mixture was added to a fluoride (potassium hexafluorotitanate) in an amount of 1% of the glass powder and simply mixed, the consistency was found to be 21 mm. On the other hand, when the glass powder was treated with the same amount of the fluoride, the consistency was found to be 30 mm. In order to examine to what extent the difference in fluidity influences the performance as an actual dental cement, the initial setting time, film thickness, and crushing strength were measured in accordance with JIS T6602 as defined for a dental zinc phosphate cement. Further, the fluidity of the cement paste was evaluated using the point of a spatula, to thereby determine the working time. The results obtained are summarized in the following table:

	<i>Powder State</i>		
	<i>No addition/ No Treatment</i>	<i>Addition with 1% Fluoride</i>	<i>Surface Treatment with 1% Fluoride</i>
Working Time	2'10"	2'05"	2'55"
Initial Setting Time	5'45"	5'30"	5'30"
Film Thickness ( $\mu\text{m}$ )	28	28	20
Crushing Strength ( $\text{kg}/\text{cm}^2$ )	1480	1570	1710

These effects are not limited to the above-specified example with respect to the glass powder formulation but are generally observed with respect to a fluoroaluminosilicate glass powder. In particular, in the present invention, the effects are remarkable with respect to a fluoroaluminosilicate glass powder obtained from the above-described raw material containing from 20 to 50% of silica, from 10 to 40% of alumina, from 10 to 50% of a fluoride, and from 0 to 20% of a phosphate. As the treatment method to be employed, any conventional treatment methods may be properly chosen and employed. Typical examples include a method in which the fluoride is dissolved in distilled water or an aqueous solution of an acid and mixed with the glass powder, followed by heating to evaporate off the water content; and a method in which the glass powder and the fluoride are well mixed and simply heated.

The glass ionomer cement is prepared by setting the fluoroaluminosilicate glass powder and polycarboxylic acid in the presence of water, and it is confirmed that a considerable amount of fluorine in the glass powder is transferred into a tooth substance. This means that a dental caries-preventing effect can be expected because the fluorine has a tooth substance-strengthening function.

As the polycarboxylic acid which sets the fluoroaluminosilicate glass powder treated with a fluoride according to the present invention, polymer acids known to be used for glass ionomer cement can be used. Examples include polyacrylic acid, acrylic acid/itaconic acid copolymer, and acrylic acid/maleic acid copolymer. These polymer acids are used in the form of either a powder or an aqueous solution. In the case that the polymer acid is used in the form of a powder, it is mixed with the fluoroaluminosilicate glass powder treated with a fluoride according to the present invention. In this case, when it is actually used in the clinical application, it is necessary to add water to set the cement.

On the other hand, in the case that the polymer acid is used in the form of an aqueous solution, an aqueous solution of the polymer acid is merely mixed with the glass powder of the present invention. Further, it is also possible that a part of the polymer acid is in the form of an aqueous solution, whereas the remainder is in the form of a powder, to mix with the cement.

In any of the above-described cases, improvers known to be used for glass ionomer cement can be used. Examples of the improver include the polybasic carboxylic acids as disclosed in Japanese Laid-Open Patent No. 101893/1977.

The invention will be further described with reference to the following illustrative Examples and

## Comparative Examples.

### Example 1

100 g of a powder of a commercially available glass ionomer cement (for cementing, "Fuji Ionomer Type I", G-C Dental Industrial Corp.) and 50 g of a 1% aqueous solution of potassium hexafluorotitanate were well mixed using a mortar. In order to completely evaporate off the water content for drying, the mixture was placed in an electric furnace set at 95°C and allowed to stand therein for one hour. Thereafter, the temperature was increased to 120°C, and the drying was carried out for an additional 2 hours.

The thus obtained powder was mixed with a setting liquid of a commercially available glass ionomer cement (for cementing, "Fuji Ionomer Type I", G-C Dental Industrial Corp.) in a proportion of a 1.4 g of the former per gram of the latter, and the initial setting time, crushing strength (after one day), and film thickness (1.5 minutes after the start of the mixing) of the mixture were measured in a thermostat at a temperature of  $23.0 \pm 0.2^\circ\text{C}$  and a humidity of  $50 \pm 2\%$  according to JIS T6602 as defined for a zinc phosphate cement. Further, the fluidity was evaluated using the point of a spatula, to thereby determine the working time. As the result of the measurements, the initial setting time, working time, film thickness, and crushing strength were 5 minutes and 20 seconds, 2 minutes and 50 seconds,  $20 \mu\text{m}$ , and  $1720 \text{ kg/cm}^2$ , respectively.

### Comparative Example 1

The physical properties of a commercially available glass ionomer cement (for cementing, "Fuji Ionomer Type I", G-C Dental Industrial Corp.) were examined in the same manner as in Example 1.

As a result, the initial setting time, working time, film thickness, and crushing strength were 5 minutes and 30 seconds, 2 minutes and 00 second,  $25 \mu\text{m}$ , and  $1420 \text{ kg/cm}^2$ , respectively.

### Example 2

42 g of silica sand, 26 g of alumina, 20 g of fluorite, 10 g of cryolite, and 2 g of calcium phosphate were mixed in a mortar, and the mixture was charged into a platinum crucible and melted at  $1250^\circ\text{C}$  for 4 hours. After the melting, the resulting mixture was cooled and then ground by means of a ball mill for 10 hours, from which a powder passing through a #150 sieve was prepared as a fluoroaluminosilicate glass powder. Separately, a 0.5% aqueous solution of zinc fluoride was prepared, and 100 parts by weight of the 0.5% aqueous solution of zinc fluoride were well mixed with 100 parts by weight of the glass powder, and the mixture was dried at  $95^\circ\text{C}$  for one hour and further at  $120^\circ\text{C}$  for 2 hours. The dried powder was sieved with a #150 sieve to prepare a sample.

The thus prepared sample powder was mixed with a commercially available dental glass ionomer cement setting liquid (for cementing, "Fuji Ionomer Type I", G-C Dental Industrial Corp.) in a proportion of 1.4 g of the former per gram of the latter. Thereafter, the physical properties were examined in the same manner as in Example 1.

As a result, the initial setting time, the working time, film thickness, and crushing strength were found to be 5 minutes and 30 seconds, 2 minutes and 20 seconds,  $21 \mu\text{m}$ , and  $1650 \pm 70 \text{ kg/cm}^2$ , respectively.

### Example 3

The fluoroaluminosilicate glass powder as prepared in Example 2 was treated with a 0.5% aluminium fluoride aqueous solution which had been previously prepared. That is, 100 parts by weight of the glass powder and 200 parts by weight of the 0.5% aluminium fluoride aqueous solution were well mixed in a mortar, and the mixture was dried at  $95^\circ\text{C}$  for 2 hours and further at  $120^\circ\text{C}$  for 2 hours. After drying, the powder was passed through a #150 sieve to prepare a sample. 80 g of the thus prepared sample was mixed with 20 g of a polyacrylic acid powder using a mortar to prepare a cement powder.

Separately, a 15% tartaric acid aqueous solution was prepared as a setting liquid. The cement powder and the liquid were mixed in a proportion of 2.0 g of the former per gram of the latter. Thereafter, the physical properties were examined in the same manner as in Example 1.

As a result, the initial setting time, working time, film thickness, and crushing strength were found to be 5 minutes and 15 seconds, 2 minutes and 50 seconds,  $21 \mu\text{m}$ , and  $1630 \pm 110 \text{ kg/cm}^2$ , respectively.

### Example 4

The fluoroaluminosilicate glass as melted in Example 2 was ground for 5 hours by means of a ball mill, passed through a #150 sieve, and then ground for an additional 5 hours to prepare a glass powder. Separately, a 1% zirconium potassium fluoride aqueous solution was prepared.

100 parts by weight of the glass powder and 200 parts by weight of the 1% zirconium

potassium fluoride aqueous solution were mixed, and the mixture was dried at 95°C for 2 hours and further at 120°C for 2 hours. After the drying, the dried powder was passed through a #150 sieve to prepare a sample. 75 g of the thus prepared sample was mixed with 25 g of a polyacrylic acid copolymer powder to prepare a cement powder.

5 Separately, a 20% tartaric acid aqueous solution was prepared as a setting liquid. The cement powder and the liquid were mixed in a proportion of 2.0 g of the former per gram of the latter. Thereafter, the physical properties were examined in the same manner as in Example 1. 5

As a result, the initial setting time, working time, film thickness, and crushing strength were found to be 5 minutes and 00 second, 2 minutes and 50 seconds, 18  $\mu\text{m}$ , and 1700 $\pm$ 90 10 kg/cm<sup>2</sup>, respectively. 10

#### Examples 5 to 7

A 2% sodium hexafluorotitanate aqueous solution was prepared as a liquid for treating the fluoroaluminosilicate glass powder as prepared in Example 4. That is, 100 parts by weight of 15 the glass powder was treated with the 2% sodium hexafluorotitanate aqueous solution in an amount of 20 parts by weight, 50 parts by weight, and 100 parts by weight, respectively. Each of the mixtures was dried at 95°C for one hour and further at 120°C for 2 hours. After the drying, the dried powder was passed through a #150 sieve to prepare a cement powder. 15

Separately, a setting liquid consisting of 40% of an acrylic acid/maleic acid copolymer (a 20 monomer ratio: 85/15), 14.5% of tartaric acid, 45% of distilled water, and 0.5% of sodium titanium fluoride was prepared as a cement liquid. 20

Each of the cement powders was mixed with the setting liquid in a proportion of 1.5 g of the former per gram of the latter. The physical properties were examined in the same manner as in Example 1. The results obtained are shown in Table 1: 25

Table 1

Example

No.	A	B	C	D	E
5	20	5'15"	2'50"	20	1740 $\pm$ 80
6	50	5'15"	3'00"	20	1750 $\pm$ 90
7	100	5'00"	3'00"	19	1780 $\pm$ 100

A: proportion of 2% Na<sub>2</sub>TiF<sub>6</sub> aqueous solution per 100 parts by weight of glass

B: initial setting time

C: working time

D: film thickness ( $\mu\text{m}$ )

E: crushing strength (kg/cm<sup>2</sup>)

#### Comparative Example 2

40 A glass powder prepared in the same manner as in Example 2, except that the 0.5% aqueous solution of zinc fluoride was not used, was mixed with the same setting liquid as in Example 2, followed by examination of the physical properties. 40

As a result, the initial setting time, working time, film thickness, and crushing strength were found to be 6 minutes and 00 second, 1 minute and 50 seconds, 26  $\mu\text{m}$ , and 1400 $\pm$ 90 45 kg/cm<sup>2</sup>, respectively. 45

#### Comparative Example 3

In Example 3, 100 parts by weight of the fluoroaluminosilicate glass powder was simply mixed with 1 part by weight of aluminium fluoride to prepare a sample. 80 g of the thus prepared 50 sample was mixed with 20 g of a polyacrylic acid powder in a mortar to prepare a cement powder. 50

Separately, a 15% tartaric acid aqueous solution was prepared as a setting liquid in the same manner as in Example 3. The cement powder and the setting liquid were mixed in a proportion of 2.0 g of the former per gram of the latter. Thereafter, the physical properties were examined 55 in the same manner as in Example 3. 55

As a result, the initial setting time, working time, film thickness, and crushing strength were found to be 5 minutes and 45 seconds, 2 minutes and 00 second, 25  $\mu\text{m}$ , and 1600 $\pm$ 60 kg/cm<sup>2</sup>, respectively.

#### 60 Example 8 and Comparative Example 4 60

In each of Example 3 and Comparative Example 3, the proportion of the cement powder to the liquid was changed to one for filling consistency, i.e. 3.2 g of the former per gram of the latter, and the initial setting time, crushing strength, and working time were measured in the same manner. The results obtained are shown in Table 2:

Table 2

	<i>Initial Setting Time</i>	<i>Working Time</i>	<i>Crushing Strength (kg/cm<sup>2</sup>)</i>	
5				5
Example 8	4'15"	2'10"	2150 ± 140	
Comparative Example 4	4'30"	1'30"	1900 ± 120	
10				10

10 It is evident from the foregoing results that the cements as prepared in Examples 1 to 7 have remarkably better properties as a dental cement as compared with those prepared in Comparative Examples 1 to 3. That is, in Examples 1 to 7, the working time is prolonged and the crushing strength is increased. Further, the thick paste cement for filling as prepared in Example 15 8 has excellent crushing strength and working time as compared with the cement paste as prepared in Comparative Example 4, which has a similar fluidity of the cement, and, therefore, the former is also an excellent dental cement.

#### CLAIMS

- 20 1. A fluoroaluminosilicate glass powder for dental glass ionomer cement, the surface of which is treated with a fluoride in an amount of from 0.01 to 5 parts by weight based on 100 parts by weight of the glass powder. 20
2. A fluoroaluminosilicate glass powder as claimed in claim 1, wherein said fluoride is a fluorocomplex salt.
- 25 3. A fluoroaluminosilicate glass powder as claimed in claim 2, wherein said fluorocomplex salt is sodium hexafluoroaluminate (Na<sub>3</sub>AlF<sub>6</sub>) or potassium hexafluoroaluminate (K<sub>3</sub>AlF<sub>6</sub>). 25
4. A fluoroaluminosilicate glass powder as claimed in any of claims 1 to 3, wherein said fluoroaluminosilicate glass powder is a fluoroaluminosilicate glass powder prepared by melting a mixed component containing from 25 to 50% of silica, from 15 to 40% of alumina, from 10 to 30 40% of a fluoride, and from 0 to 20% of a phosphate at a temperature of 1000°C or higher, followed by cooling and grinding. 30
5. A fluoroaluminosilicate glass powder as claimed in any of claims 1 to 4, wherein said glass powder is one able to pass through a #80 sieve.
6. A fluoroaluminosilicate glass powder as claimed in claim 5, wherein said glass powder is 35 one able to pass through a #150 sieve. 35
7. A fluoroaluminosilicate glass powder according to claim 1, substantially as herein described in any of the foregoing Examples.