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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
No. 05-123306- -00004-0000
Fecha: 2007-07-09 16:08:43 Dep: 2020 NUECREACIONES
Tot. 11 PATENTEJYII Eve: 379 FASENACIONALII
Act 538 PETICION Folios: 2

Clarke, Modet &
COLOMBIA

SEÑORES
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES
E.S.D

REF EXPEDIENTE No: **05 123306**
SOLICITANTES :STICHTING GLASS FOR HEALTH
TITULO: COMPOSICION DE CARBOMERO DE VIDRIO DE AUTOENDURECIMIENTO
FECHA SOLICITUD : DICIEMBRE 6,2006

ASUNTO: SOLICITUD ESTUDIO DE FONDO

DILIA RODRÍGUEZ D´ALEMAN, en mi condición de apoderada de la Sociedad solicitante, por el presente escrito atentamente solicito a Usted que habiéndose surtido la publicación de la presente solicitud, en la Gaceta de la Propiedad Industrial No.575 de fecha Abril 30 de 2007 y se proceda con el estudio de Fondo.

Para tal fin me permito anexar la tasa correspondiente.

Agradezco continuar con el presente trámite.

Señor Jefe,

DILIA RODRÍGUEZ D´ALEMAN
C.C. 41.654.882 Bogotà

P-722

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
No. 05-123306- -00004-0000
Fecha 2007-04-03
Tra 11 PATENTE/YM
Act 538 PETICION
Lva 379 PASENADONAL
Folios: 2

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 07 - 27,277
[illegible] : ABRIL 3 DE 2007

***** C O N S I G N A C I O N *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CLARKE MODET	CONSIGNACION	BANCO POPULAR	050-00110-6	63066570	03/04/2007	23,540,000.00

***** C O N C E P T O *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01 SOLICITUDES	05 EXAMEN DE PATENTABILIDAD DE INVEN	404,000.00
		TOTAL : $	404,000.00

SON: CUATROCIENTOS CUATRO MIL PESOS

RESPONSABLE : ____________________

RECIBO DE CAJA APLICADO AL EXPEDIENTE No.____________________

p 722.

Industria y Comercio
SUPERINTENDENCIA

69 69

DIVISIÓN DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. 05-123306

EL EXTRACTO DE LA PRESENTE SOLICITUD DE **PATENTE DE INVENCIÓN**

FUE PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL **No 575** DE

FECHA **30 DE ABRIL DE 2007** EL TÉRMINO HÁBIL SEÑALADO POR LA LEY

EXPIRA EL **31 DE JULIO DE 2007**

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI _____ NO ____X____

United States Patent [19]

Schmitt et al.

[11] 4,376,835

[45] Mar. 15, 1983

D1

[54] CALCIUM DEPLETED ALUMINUM FLUOROSILICATE GLASS POWDER FOR USE IN DENTAL OR BONE CEMENTS

[75] Inventors: Werner Schmitt; Robert Purrmann, both of Stuttgart; Peter Jochum, Hechendorf; Oswald Grauer, Seefeld, all of Fed. Rep. of Germany

[73] Assignee: ESPE Fabrik Pharmazeutischer Präparate GmbH, Seefeld, Fed. Rep. of Germany

[21] Appl. No.: 336,850

[22] Filed: Jan. 4, 1982

Related U.S. Application Data

[63] Continuation of Ser. No. 164,322, Jun. 30, 1980, abandoned.

[30] Foreign Application Priority Data

Jul. 18, 1979 [DE] Fed. Rep. of Germany 2929121

[51] Int. Cl.³ A61F 1/00; B32B 17/00; B32B 17/06; C08L 33/02

[52] U.S. Cl. 523/116; 65/31; 106/35; 156/663; 260/998.11; 428/375; 428/406; 428/428; 433/228; 501/39; 501/57; 501/63; 501/73

[58] Field of Search 428/406, 375; 65/31; 433/228; 156/663; 427/309; 106/35; 3/1.9; 501/39, 57, 63, 73; 523/116; 525/362; 260/998.11

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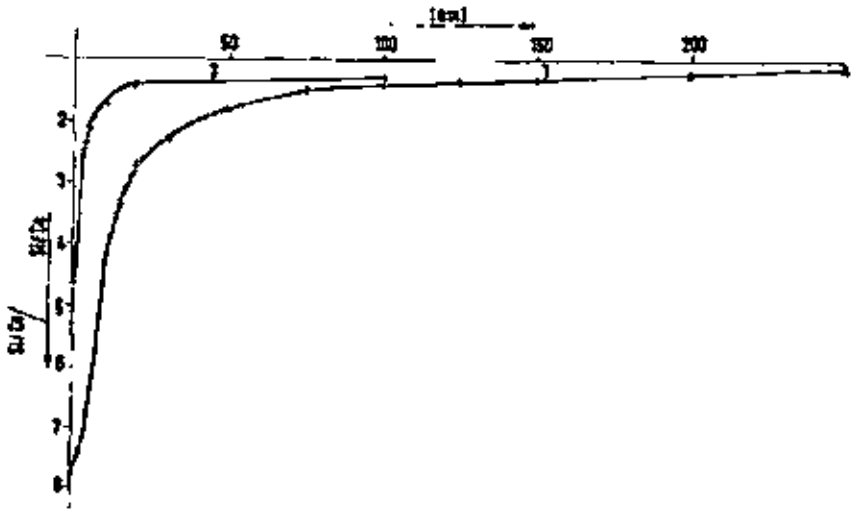
Primary Examiner—Helen M. McCarthy
Attorney, Agent, or Firm—Daley, Baumbach & Brandt

[57] ABSTRACT

A calcium aluminum fluorosilicate glass powder is disclosed which has average particle size of at least 0.5 microns, and is characterized in that the calcium in the surface of the powder's particles is depleted so that the quotient of the atomic ratio Si/Ca at the surface of the particles and the atomic ratio Si/Ca in the core region of the particles is at least 2.0, more preferably at least 3.0 and most preferably at least 4.0. The glass powder may be prepared by surface treating calcium aluminum fluorosilicate glass powder particles with an acid which forms calcium salts, washing the calcium salts off the treated particles and drying the washed particles.

The glass powder has utility in self-hardening glass ionomer cements, such as dental or bone cements. Cements formed from the glass powder exhibit reduced periods of water sensitivity, while permitting sufficient time for processing.

20 Claims, 1 Drawing Figure



CALCIUM DEPLETED ALUMINUM FLUOROSILICATE GLASS POWDER FOR USE IN DENTAL OR BONE CEMENTS

This application is a continuation of application Ser. No. 164,322, filed June 30, 1980, now abandoned.

BRIEF SUMMARY OF THE INVENTION

This invention provides a calcium aluminum fluorosilicate glass powder the particles of which have an average size of at least 0.5 microns, characterized in that the powder particles are so depleted of calcium at the surface that the quotient of the atomic ratio Si/Ca at the surface of the powder particles and the atomic ratio Si/Ca in the core region is at least 2.0 The powder may be prepared by

(a) treating a calcium aluminum fluorosilicate glass powder the particles of which have an average size of at least 0.5 microns and a maximum particle size of 150 microns with an aqueous acid solution having a concentration of 0.01 to 10% by weight;

(b) separating the treated powder from the acid solution;

(c) washing calcium salts from the surface of the separated powder; and

(d) drying the washed powder. The powder may be employed in self-hardening glass ionomer cements having utility as bone or dental cements.

BACKGROUND OF THE INVENTION

The invention relates to glass powders that may be employed in cements useful in medicine or dentistry, e.g., in bone or dental cements, especially in the so-called glass ionomer cement.

Glass ionomer cements have been described in German patent application (OS) No. 2,061,513. They consist of a calcium aluminum fluorosilicate glass powder and a mixing fluid which may generally be designated as an aqueous solution of a polycarboxylic acid. The resulting composition may be employed, for example, as a permanent filling material in dentistry. Its significance resides in the fact that it is the first tooth filling material that is satisfactory in cosmetic and mechanical respect and that is simultaneously physiologically so unobjectionable that it may be directly filled into the tooth without any underfilling and similar measures.

A disadvantage of the glass ionomer cements resides in their high water sensitivity during and after the setting reaction. While during the setting reaction the water sensitivity is hardly avoidable for principal reasons, the water resistance of the compositions after setting can be improved in two ways, namely by the use of a highly reactive powder composition or by the use of an especially reactive setting fluid. Especially favorable results are naturally obtained by the combination of the two possibilities. However, in that case the reaction is so rapid that the processing period, i.e., the period of time available for introducing the cement into the cavity and modelling it therein, is extremely short. In many cases hardening takes place already during mixing. In order to ensure sufficiently long processing time, less reactive powders and less reactive fluids are employed, so that the preparations presently available on the market are all water-sensitive for a longer period of time.

From German Pat. No. 1,267,589, it has been known to treat glass grit used in the production of porous sintered structures (filters) with bases or acids in order to cleave the surface of the glass particles.

It is an object of the invention to reduce the water sensitivity of cements useful in medicine and dentistry and based on glass powders and polycarboxylic acids while at the same time ensuring a sufficiently long processing period.

It has now been found that this object is realized when the powder component of the glass ionomer cements is a calcium aluminum fluorosilicate glass whose powder particles are on their surfaces depleted of calcium ions as compared with the average composition thereof.

Therefore, the subject matter of the invention is the calcium aluminum fluorosilicate glass powder described in the patent claims and its use.

DETAILED DESCRIPTION OF THE INVENTION

The calcium aluminum fluorosilicate glass powders of the invention preferably consist of:

Component	Calculated As	Percent By Weight
Si	SiO_2	20-60
Al	Al_2O_3	10-50
Ca	CaO	1-40
F	F	1-60
Na	Na_2O	0-10
P	P_2O_5	0-10

besides oxygen, in the core region of the powder particles, and altogether 0 to 20% by weight, calculated as oxides, of B, Bi, Zn, Mg, Sn, Ti, Zr, La or other trivalent lanthanoids, K, W, Ge, as well as further additives which do not adversely affect the properties and which are physiologically unobjectionable.

Preferably the core region of the powder particles consists of:

Si	as	SiO_2	25-30% by weight
Al	as	Al_2O_3	10-40% by weight
Ca	as	CaO	10-25% by weight
F			3-30% by weight
Na	as	Na_2O	0-8% by weight
P	as	P_2O_5	1-10% by weight

and 0 to 10% by weight of B_2O_3, Bi_2O_3, ZnO, MgO, SnO_2, TiO_2, ZrO_2, La_2O_3 or other oxides of trivalent lanthanoids, K_2O, WO_3, GeO_2 and further additives which do not adversely affect the properties and which are physiologically unobjectionable.

Especially preferred components are:

Si	as	SiO_2	25-45% by weight
Al	as	Al_2O_3	20-40% by weight
Ca	as	CaO	10-20% by weight
F			10-30% by weight
Na	as	Na_2O	1-8% by weight
P	as	P_2O_5	1-10% by weight

Regarding the empirical chemical composition in the core region of the powder particles, glasses may be used which have been described for example in German Patent Applications (OS) No. 2,061,513 or (AS) No. 2,065,824.

Examples of preferred compositions in the core region are listed in the following Table I:

TABLE I

EXAMPLES FOR THE CORE REGION COMPOSITION OF GLASS POWDERS OF THE INVENTION				
Percent By Weight	A	B	C	D
Si as SiO_2	33.0	27.6	29.0	43.4
Al as Al_2O_3	20.4	26.0	25.1	13.0
Ca as CaO	34.9	23.8	24.6	30.1
P	11.7	13.0	13.0	10.4
Na as Na_2O	2.7	2.1	2.2	0.9
F as F_2O_3	6.9	6.3	5.8	2.4

The glass powder particles of the invention are depleted of calcium at their surface such that the quotient of the atomic ratio Si/Ca at the surface of the powder particles and the atomic ratio Si/Ca in the core region is at least 2.0, preferably at least 3.0, and most preferably at least 4.0. The calcium content of the powder particles of the invention increases asymptotically from the surface to the core region.

The depth of the depletion zone depends on the conditions given in each individual case, especially on the desired processing period of the cements prepared from the glass powders of the invention. In practice it is favorable when the calcium depletion extends at least so deeply that the processing period of the mixture of the powders of the invention and the polycarboxylic acid solution is at least 1.5 min. at 23° C. In general, the depletion zone preferably extends at least to a depth of about 10 nm, more preferably to at least about 20 nm, and most preferably to at least about 100 nm. These ranges are particularly suited for use of the glass powders of the invention in dentistry. For other purposes, e.g., for use in bone cements, the depletion zone may also be deeper and may be 200 to 300 nm, for example.

As will be explained further below, the glass powders of the invention are produced by surface treatment of glass powders having a composition corresponding to the core region of the powders of the invention. Upon surface treatment the number of silicon atoms per unit volume remains substantially constant. The actual change in the absolute number of atoms per unit volume of other types of atoms is therefore obtained by forming the quotient of the relative atom proportion with the percentage silicon proportion, as is shown later by means of a practical example. The quotient of the atomic ratio Si/Ca at the surface of the powder particles and the atomic ratio Si/Ca in the core region therefore constitutes a useful value to characterize the glass powders of the invention. The accompanying figure of drawing represents a plot of the quotient of the atomic ratio Si/Ca at the point of measurement and the atomic ratio Si/Ca in the core region against the depth of the measurement for powders of the invention as described in Examples 1 and 3. The examples and FIG. 1 demonstrate that the atomic ratio Si/Ca for the individual layers of the glass powder asymptotically approaches the value of untreated starting material and thus of the core region of the treated powder.

The surface measurement to determine Ca depletion of the glass powders of the invention is suitably carried out by photo electron spectroscopy for chemical analysis (ESCA). This method has been described by R. S. Swinglo II and W. M. Riggs in Critical Reviews in Analytical Chemistry, Vol. 5, Issue 3, pages 267 to 321, 1975 and by K. Lovsen in "Chemie in unserer Zeit", Vol. 40, pages 43 to 53, 1976.

The measuring data underlying the present description were determined under the following measuring conditions of ESCA measurement:

Apparatus:	Scanning Auger ESCA spectrometer, Model PHI 550, of Messrs. Physical Electronics Industries, Munich (cf. Perkin-Elmer brochure ESCA/SAM, PHI Data Sheet 2011 2-79 Ju)
Excitation:	400 watt Mg radiator
Gold penetration energy:	100 eV
Time Constant:	0.1 sec.

The glass powders of the invention have an average particle size (weight average) of at least 0.5 microns, preferably at least 1 micron, and most preferably at least 3 microns. For dental purposes the average particle size (weight average) is 1 to 20 microns, preferably 3 to 15 microns, most preferably 3 to 10 microns. The particles have a maximum particle size of 150 microns, preferably 100 microns, especially 60 microns. For use as dental bonding cement the maximum particle size is 25 microns, preferably 20 microns. In order to achieve good mechanical properties a not excessively narrow particle size distribution is favorable, as usual, which is achieved, for example, by conventional grinding and classifying of the coarse.

The glass powders of the invention are prepared from glass powders having the average composition of the core region of the powders of the invention. To this end the glass powders described, for example, in German (OS) No. 2,061,513 and in Table I are suitable. The glass powders employed as starting materials are obtained as usual by fusing the starting components together at temperatures above 950° C., quenching, and grinding. The starting components may be, for example, the compounds stated in German (OS) No. 2,061,513 in suitable quantitative ranges.

The thus obtained powders are then subjected to a surface treatment. The powders of the invention are obtainable, for example, by removal of Ca by suitable chemical agents.

According to one embodiment of the invention the starting glass powders are treated on the surface with acid, preferably at room temperature. To this end substances containing acidic groups are employed, preferably substances forming soluble calcium salts. Sparing water-solubility of the respective calcium salts may be compensated to a certain degree by a large amount of liquid per unit of powder. The reaction period varies between a few minutes and several days, depending on the strength and concentration of the acid employed.

Thus, for instance, for the preparation of the powders hydrochloric, sulfuric, nitric, acetic, propionic and perchloric acid may be used.

The acids are employed at a concentration of 0.01 to 10% by weight, preferably from 0.05 to 3% by weight.

After the respective reaction period the powders are separated from the solution and thoroughly washed to leave substantially no soluble calcium salts on the surface of the powder particles. Finally the powder is dried, preferably above 70° C., and screened to the desired particle size ranges.

The stronger the acid employed and the longer a given acid acts on the powder the longer will be the processing period after mixing with the mixing fluid.

-continued

Processing period	2 minutes
Setting period	4 minutes
Water penetration depth (according to Example 6)	0 microns

EXAMPLE 8

A glass powder is prepared according to methods known per se (e.g., German OS No. 2,061,513) having the following composition:

Si = SiO_2	27.5% by weight
Al = Al_2O_3	20.5% by weight
Ca = CaO	25.5% by weight
Na = Na_2O	2.1% by weight
P = P_2O_5	8.3% by weight
F	17.0% by weight

A finely particulate glass powder is obtained by grinding the quenched glass composition in a ball mill.

The resulting powder is treated with 0.1% aqueous hydrochloric acid solution for 1 hour as described in Example 1. Thereafter it is passed through a screen with 20 microns sieve openings. The resulting powder is suited for use as bonding cement for artificial teeth.

To this end the resulting powder is mixed at a weight ratio of 1.8:1 with a commercial mixing fluid for glass ionomer bonding cements (Chem. Bond, A. C. International, London, England). The low viscosity mixture remains processable for about 3 minutes at room temperature and has set after 8 minutes.

EXAMPLE 9

100 grams of the powder of the invention described in Example 7 are mixed with 10.5 grams of a dry polymaleic acid powder (less than 60 microns) (prepared, for example, according to OS No. 2,101,889). From the homogeneous mixture pellets of about 200 mg (8 mm diameter, about 2 mm thickness) are produced in the conventional manner.

One of said pellets is briefly softened in 34 mg of 14% tartaric acid solution. After stirring with light pressure one obtains a homogeneous paste of good consistency which is useful as self-hardening tooth cement.

EXAMPLE 10

The powder of the invention described in Example 7 is metered in portions of 280 mg each into the mixing compartment of shaker capsules as described in German (OS) No. 1,910,835. Said capsule contains as a separate compartment a cushion of plastic-coated aluminum filled with 96 mg of an about 45% aqueous polymaleic acid solution. When using the thus prepared capsule as described in the above-mentioned (OS) and mixing the components with a mechanical mixer one obtains a cement suited as permanent filling material for tooth cavities.

EXAMPLE 11

A mixture of 285 mg of a powder of the invention corresponding to Example 7 and 35 mg of a dried maleic acid polymer is filled into the mixing compartment of a shaker capsule according to German (OS) No. 1,910,835. Said capsule contains as a separate compartment a cushion of plastic-coated aluminum filled with 54 mg of a 14% tartaric acid solution. Following the procedure described in Example 10 one obtains again a cement suited as permanent dental filling material.

EXAMPLE 12

100 grams of the powder used in Example 1 are intensively stirred with 1000 grams of 5% aqueous acetic acid solution for 2 hours. Thereafter the slurry is filtered, thoroughly washed, dried for 2 hours at 120° C. and screened to a particle size of less than 60 microns.

After mixing with about 45% polymaleic acid solution in a weight ratio of 2.5:1 a cement composition is obtained which remains processable for about 5 minutes and which has set after 8 minutes.

This cement composition is especially well suited as bone cement, e.g., for bonding artificial hip joints.

What is claimed is:

1. A calcium aluminum fluorosilicate glass powder reactable with a mixing fluid to form a self hardening glass ionomer cement exhibiting properties of reduced period of water sensitivity and at the same time insuring a sufficiently long processing period, said glass powder being characterized by particles having an average size of at least 0.5 microns, and in that the level of calcium present at the surface of the powder particles is depleted relative to the level of the calcium present in the core region and to the extent that the quotient of the atomic ratio Si/Ca at the surface of the powder particles and the atomic ratio Si/Ca in the core region is at least 2.0, with the calcium content increasing asymptotically from the surface to the core region.

2. The glass powder of claim 1 having a core region comprising:
- 20–60 weight percent SiO_2,
- 10–50 weight percent Al_2O_3,
- 1–40 weight percent CaO,
- 1–40 weight percent F,
- 0–10 weight percent Na_2O, and
- 0–10 weight percent P_2O_5.

3. The glass powder of claim 2 further comprising 0–20% by weight of an oxide of the group consisting of B, Bi, Zn, Mg, Sn, Ti, Zr, La, a trivalent lanthanide, K, W and Ge.

4. The glass powder of claim 3 wherein the oxides are selected from the group consisting of B_2O_3, Bi_2O_3, ZnO, MgO, SnO_2, TiO_2, ZrO_2, La_2O_3, K_2O, WO_3 and GeO_2.

5. The glass powder of claim 2 having a core region comprising:
- 25–50 weight percent SiO_2,
- 10–40 weight percent Al_2O_3,
- 10–35 weight percent CaO,
- 5–30 weight percent F,
- 0–8 weight percent Na_2O, and
- 1–10 weight percent P_2O_5.

6. The glass powder of claim 5 further comprising 0–10 weight percent of an oxide of the group consisting of B, Bi, Zn, Mg, Sn, Ti, Zr, La, a trivalent lanthanide, K, W and Ge.

7. The glass powder of claim 2 having a core region comprising:
- 25–45 weight percent SiO_2,
- 20–40 weight percent Al_2O_3,
- 10–30 weight percent CaO,
- 10–30 weight percent F,
- 1–8 weight percent Na_2O, and
- 1–10 weight percent P_2O_5.

8. The glass powder of claim 1 wherein the quotient is at least 3.0.

9. The glass powder of claim 1 wherein the quotient is at least 4.0.

10. The glass powder of claim 1 wherein the surface calcium depletion extends to a depth of at least about 10 nm.

11. The glass powder of claim 10 wherein the depletion extends to a depth of at least 20 nm.

12. The glass powder of claim 10 wherein the depletion extends to a depth of at least 100 nm.

13. The glass powder of claim 10 wherein the depletion extends to a depth of about 200-300 nm.

14. The glass powder of claim 1 wherein the average particle size is at least 1 micron.

15. The glass powder of claim 1 wherein the average particle size is at least 3 microns.

16. The glass powder of claim 1 wherein the maximum particle size is 150 microns.

17. The glass powder of claim 1 wherein the maximum particle size is 100 microns.

18. A self-hardening glass ionomer cement comprising an aqueous mixture of the calcium aluminum fluorosilicate glass powder of claim 1 having a maximum particle size of 150 microns, a polycarboxylic acid and chelating agent.

19. The cement of claim 18 wherein the average particle size of the powder is 1-20 microns and the maximum particle size is 100 microns.

20. The cement of claim 19 wherein the average particle size of the powder is 3-10 microns and the maximum particle size is 60 microns.

21. The cement of claim 18 wherein the maximum particle size is 25 microns.

22. The cement of claim 18 wherein the maximum particle size is 20 microns.

23. A dental filling material comprising the cement of claim 18.

24. A dental filling material comprising the cement of claim 19.

25. A dental filling material comprising the cement of claim 20.

26. A dental filling material comprising the cement of claim 21.

27. A dental filling material comprising the cement of claim 22.

28. A dental bonding cement comprising the cement of claim 21.

29. A bone cement comprising the cement of claim 18.

30. A dental bonding cement comprising the cement of claim 22.

* * * * *

United States Patent [19]

Pollak

[11] **4,449,938**

[45] **May 22, 1984**

D2

[54] **ENDODONTIC FILLING AND SEALING COMPOSITION**

[75] Inventor: Richard B. Pollak, Los Angeles, Calif.

[73] Assignee: Lee Pharmaceuticals, Inc., So. El Monte, Calif.

[21] Appl. No.: 850,404

[22] Filed: Feb. 19, 1982

[51] Int. Cl.³ A61K 6/08

[52] U.S. Cl. 523/116; 106/35; 260/998.11; 433/228; 523/117; 524/731; 528/18; 528/34; 528/901

[58] Field of Search 433/228; 106/35; 260/998.11; 523/115-118; 524/731, 901; 528/18, 34

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Primary Examiner—Lorenzo B. Hayes
Attorney, Agent, or Firm—Joseph E. Maeth

[57] **ABSTRACT**

A biologically compatible non-toxic composition which when mixed, is useful as an in situ curing endodontic filling material. The composition has two separately packaged components. One component is a paste which contains a low viscosity hydroxy terminated polydialkylsiloxane and a non-reactive silicone oil diluent having a viscosity of from about 20 to 20,000 centistrokes at 25° C. and comprising a polydialkylsiloxane. The other component is a liquid which includes (i) the reaction product resulting from the refluxing at ambient pressure and a temperature of about 150° to about 175° C. under a nitrogen blanket in the absence of air and moisture a dialkyltindicarboxylate in which the alkyl groups have from 1 to about 8 carbon atoms and the carboxylate groups contain from about 10 to about 18 carbon atoms and a tetraalkyl orthosilicate, in the molar ratio of 1 to 3; (ii) unreacted alkyl orthosilicate and (iii) a non-reactive silicone oil diluent having a viscosity of from 20 to 120,000 centistrokes at 25° C. and comprising a polydialkylsiloxane.

The method of treating a root canal in need of endodontic filling which comprises the steps of forming a mixture by thoroughly mixing, with each 1.5 grams a paste component, 5 to 6 drops of the liquid component. The resulting mixture is injected by syringe or hypodermic needle into an endodontically prepared root canal and allowed to stand for about thirty minutes and harden in situ to form a flexible soft non-toxic filling material which conforms to the shape of the root canal cavity.

12 Claims, No Drawings

ENDODONTIC FILLING AND SEALING COMPOSITION

This invention relates to an endodontic filling and sealing composition. More specifically, the invention relates to a non-toxic, non-irritating endodontic filling and sealing composition which is inert to tooth structure and surrounding tissue which comprises a composition which is formed in situ in the root canal and which, prior to setting is of a viscosity enabling easy injection from a hypodermic needle.

BACKGROUND OF THE INVENTION

A practical endodontic filling composition has numerous requirements. It must not shrink excessively on setting, thus unsealing the root canal. It must set within a time which reasonably permits completion of endodontic procedure without undue patient discomfort. It must be biologically compatible with tooth structure and non-toxic. It must be inert to moisture and to the acid-base conditions found in the mouth. Is is preferably X-ray opaque. It should also be of low viscosity to facilitate ready insertion into and complete filling of the canal itself prior to setting. It should be easy to remove after setting if necessary or desirable. To permit insertion and retention in root canals of upper teeth before curing, it must be thixotropic. It should not discolor or stain tooth structure on prolonged residence in the mouth.

Systems which can be injected by means of a syringe have also been used as endodontic filling materials. One such system uses zinc oxide and eugenol. The two materials are mixed together to form a paste. This can be placed into a pressure syringe and injected into the root canal. The zinc oxide-eugenol mixtures polymerize when initiated by water. This material is a poor choice for several reasons. Adhesion to the walls of the canal is very low. It is very soluble and has little physical strength. It does not penetrate secondary canals.

A mixture of hydroxyethyl methacrylate, fillers and catalysts has also been used as a syringeable endodontic filler since the monomer cures to a rigid plastic, which, after a few days, absorbs enough water to become a soft hydrogel. However, hydroxyethyl methacrylate is a serious skin irritant. The residual catalysts are also believed to be irritating. This material relies on the absorption of water to swell up and seal the canal so the seal is often incomplete.

Similarly, compositions based on epoxy resins have been employed as injectible endodontic filling materials. One such material, known as AH26, consists of an epoxy resin (diglycidyl ether of bisphenol A), fillers and hexamethylene tetramine. Although epoxy resin are generally considered to cure hard and rigid, this system cures slowly to a weak material. The epoxy resin is a bad skin irritant and sensitizer. The formaldehyde released in the presence of water by the breakdown of the hexamethylene tetramine is both an antiseptic and an irritant. Because of these drawbacks the material has not found widespread use.

Two part room temperature setting silicone compositions comprising a base material and a catalyst and the use thereof as dental impression material is described, for example, in U.S. Pat. Nos. 4,007,123 and 3,897,376. The base material of U.S. Pat. No. 4,007,123 comprises a hydroxy dimethyl siloxane, an organo-silicone cross-linker, and a unique filler, the catalyst component of which is a metal salt of a carboxylic acid, e.g., tin linoleate, stearate, oleate, acetate, or butyrate.

Two-component, room temperature setting organopolysiloxane compositions comprising (i) a hydroxy terminated diorganopolysiloxane mixed with a filler and (ii) a catalyst mixture of a tin carboxylate and an alkyl silicate or partially hydrolyzed alkyl silicate are described in U.S. Pat. No. 2,843,555. According to U.S. Pat. No. 3,897,396, it has been suggested that such two part compositions be placed in a syringe or other device and inserted from the device into the ear so that the composition can cure in situ to form an ear plug for the attenuation of sound.

Silicone compounds said to be useful as dental molding compounds and for filling tooth roots are described in British Pat. No. 841,825. U.S. Pat. No. 3,062,526 describes a single component, water or saliva, cured silicone rubber system for filling root canals.

Silicone elastomers have been proposed for use as endodontic filling and sealing compositions. Such endodontic products so proposed were not formulated to enable application as a flowable liquid by a disposable syringe, e.g., a hypodermic syringe. Nor do prior writings concerning such proposals affirmatively show the achievement of a non-toxic root canal filling material inert to surrounding tissues and to mouth conditions, though it is to be recognized that such has necessarily been the desideratum.

For example, Nitzsche U.S. Pat. No. 3,127,363 describes a polysiloxane elastomer which cures at room temperature. The patent states that certain of the disclosed compositions are "especially suitable as root fillings for decayed teeth . . . because within a few minutes after having been pressed into the root channel they set to form a solid though still elastic mass . . . " (Col. 8, lines 33–40). Hydroxy terminated polysiloxanes are utilized as starting materials for polymerization with various metal salt catalysts including dibutyltin dicarboxylates. The Nitzsche patent discloses the use of cross-linking agents, but prefers such agents to be siloxanes present in relatively low amounts based on the weight of hydroxy terminated polysiloxane utilized. The patent discloses that "in certain circumstances" polyalkyl silicates may be used as cross-linkers (Col. 3, line 67–Col. 4, line 37), but lists numerous disadvantages connected with their use. In particular, greater shrinkage upon reaction of the hydroxy terminated polysiloxanes with cross-linkers is said to inhere if "polyethyl silicate" is the cross-linker than if $RSi(OR)_3$ or $RSi(OR)_2$ is so employed (Col. 4, lines 14–20). No particular formulation is exemplified as useful for root canal fillings. No reference is made to non-cross-linked compositions of a viscosity requisite to permit injection by syringe into the root canal. Some catalyst compositions of the type described in Nitzsche and the polymer obtained therefrom have been found to be biologically unacceptable.

Lewis U.S. Pat. No. 3,186,963 describes gelling a dimethyl polysiloxane at room temperature with a "vulcanizing agent" catalyst system which is a reaction product of a tin salt of carboxylic acid, e.g., dibutyl tin dilaurate and a silicate, e.g., ethyl orthosilicate. The reaction of the tin salt and the alkyl silicate is performed under ambient atmospheric conditions at 80° to 200° C. for at least 15 minutes, or under what the examples call "reflux" conditions using the same time and temperature criteria. The examples show that when an alkylpolysilicate is substituted for ethylorthosilicate, the

catalyst similarly prepared can be "diluted" with excess alkyl polysilicate, but Example 2 indicates that the gel time is lengthened when such "diluent" is present relative to an equivalent mix containing no diluent. No information is given with respect to the viscosity of the catalyst, diluted or undiluted, or of the dimethyl polysiloxane starting material. No information is given about the characteristics of the gelled composition. Nor is reference made to the use of the composition as a root canal filling and sealing material.

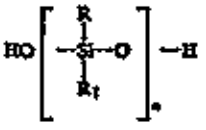
Smith U.S. Pat. No. 3,957,704 describes unique cross-linking agents for two component room temperature vulcanizable silicone rubber compositions. These cross-linking agents are said to solve certain problems which attend the compositions of Lewis U.S. Pat. No. 3,186,963; namely variation in the cure rate and instability of the activity of the catalyst component upon storage. Dilution of the Lewis reaction product catalyst with a non-reactive dimethylpolysiloxane chain stopped with triorganosiloxy units is said to degrade the catalyst component seriously in that the shelf life was less than one to two months.

BRIEF DESCRIPTION OF THE INVENTION

The present invention is a two component endodontic filling and sealing composition which is non-toxic, inert to tissues, including tooth tissues adjacent a root canal, inert to mouth conditions, non-discoloring upon aging, exhibits essentially no shrinkage upon curing and is of a viscosity prior to curing such that it can be placed in the root canal with a disposable syringe.

The essential ingredients of this novel filling and sealing composition are:

(1) a low viscosity hydroxy terminated polysiloxane of the general formula:



I.

wherein R and R_1 are each alkyl groups of from 1 to about 4 carbon atoms which may be the same or different and n is an integer of from about 8 to about 160;

(2) a catalyst prepared by reacting (a) a dialkyl tin dicarboxylate in which the alkyl groups have from 1 to about 8 carbon atoms and the carboxylate groups have from about 10 to about 18 carbon atoms with (b) tetraalkyl orthosilicate, by heating (a) and (b) in the molar ratio of 1 part (a) to about 3 parts of (b) under an atmosphere of nitrogen, and under conditions such that water and moisture are rigorously excluded, for at least about one hour at a temperature from about 150° to 175° C.;

(3) a biologically acceptable cross-linking agent, preferably ethyl orthosilicate. Uncombined tetraethyl orthosilicate is preferred;

(4) a fluid silicone oil having a viscosity of from about 20 to 120,000, preferably about 12,500 centistokes when measured at 25° C. comprising a di(lower alkyl) siloxane in which the alkyl groups have from 1 to about 3 carbon atoms—e.g., poly(dimethylsiloxane)—which functions at least mainly as a diluent.

X-ray opaquing agents such as barium sulfate, suitable pigments (e.g., zinc oxide; red iron oxide), fillers, medicaments, antioxidants, etc., may be included in the endodontic formulation as desired.

The endodontic filling and sealing material is formulated as two separately packaged components to be mixed immediately prior to injection into the root canal. A preferred system is one in which a base component comprising ingredient (1) is formulated as a paste composition which may also contain ingredient (4) as needed, desired pigments, X-ray opaquers, medicaments, etc., while ingredients (2), (3) and a further increment of (4), as needed, are formulated as a separate, liquid catalyst composition.

In the paste composition, the ingredient (1) is usually provided in an amount of 20 to 70% by weight of said paste, preferably 25–50% and even more preferably 30–40%. Ingredient (4) may be included in the paste in an amount up to about 70% by weight based on the weight of ingredient (1).

In the liquid, catalyst-containing composition, ingredient (2) constituting the catalyst comprises from about 5 to about 30%, preferably about 10–15% by weight of said liquid composition; ingredient (3), tetraalkyl orthosilicate, comprises from about 40% to about 60% by weight of the liquid composition, and preferably 50–55% by weight; and ingredient (4) comprises from about 15 to about 45%, by weight preferably about 30–35% by weight of the liquid composition.

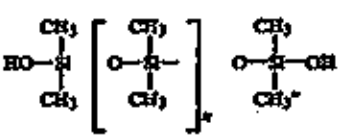
In use, the two components are mixed in a ratio suitable to provide a low viscosity injectable liquid with a set time of about 20 to 60 minutes, injected into the prepared root canal, and allowed to set. Usually, about 5–6 drops of liquid catalyst composition, each of which weighs about 0.016 gram, are mixed with about 1.5 grams of paste to form a liquid that is readily injectable, suitably thixotropic and of proper set time to permit the dentist to perform any needed manipulations before the composition cures. About five to six drops of liquid catalyst composition are required for each 1.5 grams of paste to provide a mix with a working time of at least 30 minutes.

DETAILED DESCRIPTION OF THE INVENTION

The essential ingredients are first described in detail:

The Hydroxy Terminated Polysiloxane—Ingredient 1

Among the suitable hydroxy terminated polysiloxanes which are commercially available are a preferred type available from Mobay Chemical Corporation under the trade name Baysilone Polymer C. A Mobay "Product Information" bulletin states that "Baysilone Polymer C" is the name used for a group of polydimethylsiloxanes having terminal OH groups and the following general formula



Baysilone Polymer C is available in various grades having a viscosity in centistokes at 20° C. as follows:

Grade	C-0.7	C2	C5

-continued

Viscosity	600-800	1800-2200	4200-6000

The lowest viscosity grade C-0.7 is preferred.

The Catalyst—Ingredient 2

The catalyst is prepared by heating a mixture of from about 20 to 80 weight percent of a dialkyl tin carboxylate and from about 80 to 20 weight percent of a tetraalkyl orthosilicate under reflux at about 150° to 175° C. atmospheric pressure for a time period of from one to four hours. It is essential for purposes of this invention that air and moisture be excluded during this reaction. Preferably the reaction is conducted under a nitrogen blanket. Preferably the catalyst reaction mixture contains, in substantially stoichiometric proportions, from about 35 to about 65 weight percent of dialkyl tin carboxylate and about 65 to about 40 weight percent of alkyl orthosilicate, i.e., about one mole dialkyl tin carboxylate for each three moles of ethyl orthosilicate.

The dialkyl tin carboxylate must be selected with care to avoid the formation of a carboxylic acid by-product which is an irritant or otherwise biologically unacceptable. For the purposes of this invention, dialkyl tin dilaurate is preferred. Other tin salts which yield biologically acceptable acid by-products include dialkyl tin oleate, linoleate, palmitate and stearate. Dialkyltindiacetate yields acetic acid, a toxic irritant, as a reaction by-product and hence does not provide a useful catalyst.

The alkyl orthosilicate is preferably selected to avoid the formation of a biologically unacceptable alcohol reaction product such as methyl alcohol but also to yield an alcohol reaction product which is absorbed without adverse effect in the cured endodontic filling. Alternatively the alcohol may be distilled off or vented after the catalyst reaction is completed. Tetraethyl orthosilicate is preferred. Tetra-n-propyl or tetra-n-butyl silicate or other suitable alkyl orthosilicates may be used.

The Cross-Linking Agent—Ingredient 3

A preferred cross-linking agent is uncombined tetraethyl orthosilicate. The ethyl alcohol by-product is non-toxic and is absorbed in the cured endodontic filling.

The Silicone Oil—Ingredient 4

The polydimethylsiloxane silicone oil ingredient is free of hydroxyl or other reactive end groups and does not participate in the curing reaction. Its purposes are many and include to dilute the catalyst to the desired concentration, to reduce viscosity of the combined base and catalyst mixture sufficiently to permit easy dispensing from a hypodermic needle, to reduce viscosity of the base composition, to protect the base and liquid compositions from moisture during storage, to plasticize the cured root canal filling, etc.

The preferred poly(dimethylsiloxane) oil is obtained as Dow Corning 360 Medical Fluid. The Dow Corning Corporation Medical Products Bulletin 51-374A dated May 1979 states that 360 Medical Fluid is a clear, colorless, polydimethylsiloxane liquid available in various viscosity grades including 20, 100, 350, 1000 and 12,500 cs at 25° C. For the purposes of this invention, the highest viscosity, 12,500 cs grade, is preferred. Other comparable poly(dimethylsiloxane) oils from other manufacturers may also be used so long as they are of appropriate viscosity.

Inert diluents other than polydimethylsiloxanes and which afford acceptable biological response may also be used. Industrial grades of silicone oils such as General Electric SF-69 are biologically unacceptable.

The silicone oil is utilized in an amount requisite to adjust the viscosity of the endodontic formulation to a level appropriate for syringe injection into the root canal.

Any excess of that required to provide an endodontic product of the desired viscosity is to be avoided to preclude undue flexibility and softness in the cured product. If more than about 50% by weight of silicone oil, based total weight, is present in the liquid component, its stability will be adversely effected.

Dilution with silicone oil also retards the rate of reaction between the base and catalyst components and impairs the flexibility of the cured product. For these reasons and to avoid bleeding of the diluent out on the surface of the cured mixture, no more than 50% weight percent of silicone oil based on ingredient 1 is utilized.

Flexibility of the cured endodontic filling and sealing composition is measured by mixing the base and catalyst components to form a paste and applying the paste with a 0.003 inch Bird Film applicator to a Q-Panel (a 3 inch×6 inch×0.01 inch tin-plated steel panel). After the paste is cured on the panel, the panel is bent over a ¼ inch steel mandrel. If cracks appear visual to the eye, the material is said to fail the ¼ inch bend test. Progressively larger mandrels may be used, if desired, to determine the size at which cracking does not occur.

Other Ingredients (Optional)

Other ingredients which may be included, as desired, are pigments, X-ray opaquers, medicaments, and thickening agents, cure retardants, cure accelerators, etc.

Pigments and X-ray opaquing agents, in general, also act as thickeners. Other additives may also perform dual functions in these formulations.

Among the pigments suitable for imparting a white color to the otherwise colorless cured root canal filling material of this invention are zinc oxide and titanium oxide, the first of which has a retardant effect upon initial set (or gelation) of the mix, thus allowing more working time to the endodontist, but an acceleration effect upon final cure. A preferred zinc oxide is U.S.P. No. 12 from New Jersey Zinc Division of Gulf and Western Industries. A preferred titanium dioxide is U.S.P. grade of about 0.3 micron average particle size.

When a flesh color is desired in the final product, red iron oxide may be added. A preferred form of this pigment is Atlas A6235 from H. Kohnstamm & Co., an approved drug and cosmetic color.

A preferred X-ray opaquing agent is natural barytes, such as Barytes 300 OC from Smith Chemical Co.

Care must be taken in selecting particulate additives that are so sized as not to clog the syringe used to place the mix in the root canal and that their properties are such that they do not tend to clump, but can easily be uniformly mixed.

In order to obtain a convenient setting time, and still insure a thorough cure, it is preferred to add up to 2 weight percent of a retardant comprising an alkanoic acid, preferably one with tail branching having from about 8 to 12 carbon atoms. The preferred alkanoic acid is neodecanoic acid. It has been found that alkanoic acids of too few carbon atoms impart odor problems to

the mix during cure, whereas those with too many carbon atoms are incompatible with the cured final composition and tend to bleed out.

EXAMPLE 1

Preparation of the Paste Component

211.5 grams of Mobay Baysilone Polymer C-0.7 is placed in a mixing bowl of a Hobart Mixer. 500.0 grams zinc oxide U.S.P., 150.0 grams barium sulphate and 3.2 grams synthetic red iron oxide were gradually added to the polymer under agitation. 135.3 grams of polydimethyl siloxane (Dow Corning 360 Medical Fluid, 20 cs) were gradually added to yield a paste. The paste is ground with two passes on a roller mill at the one dot position to obtain a No. 4 grind on the Hegman scale on a Precision Gauge and Tool Fineness of Grind Gauge, as specified in ASTM Method D1210. The paste was then strained through an 80 mesh nylon bag.

Preparation of the Liquid Catalyst Component

A mixture of 100 grams of dibutyl tin dilaurate and 100 grams of tetraethyl orthosilicate was reacted under reflux for two hours at a temperature of about 100° C. The reaction product was cooled and filtered through Whatman No. 1 paper. 133.2 gms of the reaction product catalyst was combined with 535.5 gms of tetraethyl orthosilicate and 330 gms of polydimethylsiloxane (Dow Corning 360 Medical Fluid, 20 cs).

Combination of the Liquid and Paste Components to Provide an Endodontic Filling Composition

About 1.5 parts by weight of the paste component were combined with about 1 part by weight of the liquid catalyst component to provide a smooth thixotropic composition injectable into a root canal through a 30 gauge needle. This composition set in approximately 30–35 minutes to a smooth soft rubber characterized by a Shore A hardness of about 3. This cured product also readily passed the ⅛" mandrel bend test.

Injection of the Endodontic Composition Into a Root Canal

The root canal to be filled is cleansed and enlarged using traditional endodontic procedures. The canal is irrigated with sterile water and dried with paper points. Five drops of catalyst component (approximately 75 mg. reaction product of 0.21 millimoles of tetraethyl ortho silicate and 80.0 micromoles of dibutyl tin dilaurate), and 1.5 grams of base component (0.23 millimoles of Baysilone C-0.70) of paste are dispensed into a glass mixing slab. Since two moles of Baysilone C-0.70 react with one mole of tetraethyl orthosilicate there is twice as much cross linking agent as is stoichiometrically required. The liquid and paste are spatulated together until a uniform mix is obtained, about 30 seconds. This mixture is immediately inserted into a syringe and injected into the root canal. The canal is full when a small amount of the filling material appears at the preparation access. After about thirty minutes the material sets.

Variation in Liquid/Paste Ratio to Adjust Set Time

The practitioner can adjust the set time of the material by varying the ratio of catalyst to base used. Using the material from Example 1, the set time is varied according to the following table when used with 1.5 grams of the paste from Example 1.

Drops Catalyst	Micro-moles DBTDL	Milli-moles TEOS	ADA Set Time at 23C*
4	63.3	.172	41 minutes
5	79.1	.216	24
6	93.0	.259	13

*American National Standard Z161.19-1977 paragraph 4.3.4.
TEOS = Tetraethyl ortho silicate
DBTDL = Dibutyl tin dilaurate
One drop equals 0.017 grams of catalyst

The use of less than 30 micromoles of dibutyl tin dilaurate and 0.08 millimoles of tetraethyl orthosilicate for each 0.21 millimoles of Bayslone C-0.70 yields a material which does not cure after 100 hours. If more than six drops, 93.0 micromoles of dibutyl tin dilaurate and 0.259 millimoles of tetraethyl orthosilicate are used, the material will set too quickly to be used in root canal treatment.

Increase in Cure Rate by Water Addition

Addition of a small amount of water to the mixture prepared in Example 1 does not significantly change the handling properties of the material but increases the cure rate and the thoroughness of the cure. To 1.50 grams of paste 0.00375 grams (0.208 millimoles) of distilled water was added. Set time was measured for material with varying amounts of catalyst at 23C and 37C.

Drops Catalyst	Micro-moles DBTDL	Millimoles TEOS	ADA Set Time 23C	ADA Set Time 37C
2	31.6	.086	—	121.0 min.
3	47.5	.130	44.5 min.	27.4
4	63.3	.173	22.5	14.5
5	79.1	.216	19.2	12.1
6	93.0	.259	13.0	8.1
7	110.8	.302	10.3	—

Moles B C-0.7/ Mole Water	Moles DBTDL Mole Water	Moles TEOS/ Mole Water	Set Time 37C
0.9	0.132	0.413	121.0 min.
0.9	0.228	0.625	27.4
0.9	0.326	0.832	14.5
0.9	0.380	1.09	12.1
0.9	0.456	1.24	8.1

A set time of less than fifteen minutes or more than sixty minutes will be difficult to use. In this example, water is added to the mixture in the proportion of 0.9 moles per mole of Bayslone C-0.70.

EXAMPLE 2

Preparation of the Paste Component

350 grams of Bayslone Polymer C-0.7 were combined in the bowl of a Hobart mixer gradually and with continuous stirring with 150.0 grams of titanium dioxide, 400 grams of barium sulfate, and 0.32 gram of red iron oxide. The paste so formed was ground with two passes on a three-roll mill to obtain at least a No. 4 grind as explained in Example 1. 90.03 grams of the ground product was combined with 9.97 grams of Polymer C-0.7, 0.10 grams of neodecanoic acid and 0.5 grams of deionized water. This mixture was stirred to provide a smooth homogeneous paste which was thereafter screened through an 80 mesh nylon screen.

Preparation of an Endodontic Filling and Sealing Material

15 parts of the paste component as described in this Example was combined with one part by weight of the liquid catalyst component as described in Example 1 but containing 12,500 gs silicone oil to produce a smooth thixotropic mass readily injectible through a 30 gauge needle. This product sets in approximately 35 minutes to a smooth soft rubber with cured properties similar to those of the cured product in Example 1.

The product of this Example 2 is a particularly preferred embodiment of the present invention.

EXAMPLE 3

85.33 grams of the ground paste described in Example 2 is mixed with 13.85 grams of Polymer C-0.7, 0.32 grams of fumed silica and 0.050 grams of distilled water to provide a smooth homogeneous paste which is thereafter screened through an 80 mesh screen. A mixture of 15 parts of such paste with one part of the liquid catalyst component described in Example 1 provided a smooth thixotropic mass injectable through a 30 gauge needle which sets in approximately 45 minutes.

Biological Compatibility

The unmixed paste composition, the unmixed liquid composition, the freshly mixed but uncured total composition and the cured total composition have all been subjected to various tests on animals as detailed hereinafter. The various test methods employed are as follows:

(a) Mucous Membrane Irritation in Mice

The procedure was adapted from a test to examine the irritation potential of contraceptive preparations. The material is placed in the vaginas of virgin mice for 24 hours after which the tissue is examined microscopically for irritation response. All components of the endodontic filler were examined: the catalyst alone, the base alone, and the freshly mixed combination of the catalyst and base (implanted before polymerization).

(b) Muscle Implants in Rabbits

This procedure generally follows the USP procedure for muscle implants. The material is inserted using a hypodermic needle into the paravertebral muscles of the rabbit. Usually the test material was placed in three to four sites on one side of the spine and the control in a similar number of sites on the other side. The usual duration of the test was one week, although some were carried out for six weeks. After that time, the sites were exposed and examined for gross responses. In the latest testing histological studies of the tissue around the sites have also been conducted.

(c) Acute Toxicity in Mice

The procedure involves making standard size samples of polymerized material and extracting them in either normal saline or polyethylene glycol at prescribed temperatures and times. The extract is then injected either i.p. (in the abdominal cavity) or i.v. (in the blood stream) of mice. The animals are observed for toxic responses and survivors are sacrificed and subjected to autopsy. The USP sets standards for passing or failing the test.

(d) Hemolysis on Rabbit Blood

Again standard size samples are made and incubated with a diluted solution of rabbit blood in normal saline. After incubation, the saline solution is centrifuged and the supernatant examined spectrophometrically for red cell lysis. Standard controls are used and a percentage hemolysis of 5% or less is considered passing.

(e) Oral Toxicity (LD-50) in Mice

The oral toxicity test is a standard test procedure consisting of administering the material orally to mice and estimating the lethal dose for half the population. This test was not used as a screening test but for safety and handling information for the catalyst. The base was not examined because of the thick nature of the material and the general inactivity of the ingredients.

(f) Embryo Implants in Chickens

The procedure required 18 day old fertile chicken eggs. A "window" was cut in the egg and the test material implanted in the muscle of the embryo wing. The egg was then resealed and allowed to hatch (the hatch rate was also dependent on the material implanted). About 11 days after hatching the sites were examined grossly and histological preparations were made.

(g) Endodontic Usage Tests in Dogs or Rats

The endodontic usage tests were tests using dogs (and in one case rats) in which normal root canal preparations were made and after prescribed time periods, the periapical tissue was examined for irritation response.

(h) Open Epicutaneous Test or "OET" (Various Animals)

The OET (open epicutaneous test) consists of 21 daily topical applications followed by challenge applications for sensitization response.

(i) Guinea Pig Maximization Test ("GPMT")

This test consists of a one time injection of the material and an adjuvant plus a single topical application, followed by a two week "rest" before challenge for sensitization response.

Biological testing data is set forth in the ensuing table.

The following table summarizes biological tests conducted on the product of Example 1 or at least one of its components.

Test Section	Type of Test	Material Tested	Summary Of Results
599	GPMT	Catalyst Component	In Progress
598	LD-50 (Mice)	Catalyst Component	In Progress
597	OET	Catalyst Component	In Progress
594	Chicken Implants	Fresh Mix	Moderate response in comparison to zinc oxide - eugenol (severe) and gutta percha (mild to none)
591	Hemolysis	Cured Mix	Passed test in contrast to zinc oxide - eugenol which after one day's curing failed by large margin.
589	Muscle Implants	Fresh Mix	No adverse response seen by gross observation. In slides, mild to moderate

-continued

Test Series	Type of Test	Material Tested	Summary Of Results
			response were which compares favorably to mild response seen with U.S.P. plastic.
537	Chicken Implants	Fresh Mix	Compared to zinc oxide - eugenol (worst response) and U.S.P. negative control plastic (mild response) showed moderate response (thin capsule, moderate infiltrate)
536	Muscle Implants	Fresh Mix	No adverse response seen macroscopically. Thin capsules and some infiltrate seen in histological preparations.
571	Rabbit Mucous Membrane Irritation	Catalyst Component	Compared to 70% ethanol, provoked very mild to no response
565	Muscle Implants	Fresh Mix	Neither implants with normal amount of catalyst nor those with twice normal amount provoked gross signs of irritation. Histology revealed mild response.
567	Modified Draize (Rabbit)	Base Component and Catalyst Component Separately	The base was not an irritant. The catalyst was mildly irritating
677	Endodontic Usage (dogs)	Mix	Compared to "Hydron" a commercial root canal filler of Kerr Co., provoked some moderate response with microabscesses, apparently resolving.
430	Antimicrobial activity	Base Component	3 of 4 microorganisms inoculated into base were viable after 48 hours.
—	microscopic examination	Cured Mix	Compared favorably with "Hydron" when extracted teeth filled with each were examined under light and scanning electron microscopes.
453	Microbial Inhibitor	Base Component, Catalyst Component and Cured Mix Separately Tested	None inhibited bacterial growth
444	Muscle Implants	Fresh Mix and Cured Mix each tested separately	Compared to "Hydron", which exhibited mild response, product of Example 1 showed no adverse response after 1 week. Photographs on file.
442	Hemolysis	Cured Mix	Compared to "Hydron" which showed 43.1% average hemolysis, Example 1 product showed 1.28% average hemolysis.
437	Hemolysis	Cured Mix (Normal catalyst amount and twice normal catalyst amount)	In U.S.P. and FDA test methods, average hemolysis for both batches was less than 3%.
434	Extraction in Normal	Cured Mix	Passed U.S.P. Test in normal saline;
	saline and polyethylene glycol		test in polyethylene glycol inconclusive and should be repeated.
433	Muscle Implants	Fresh Mix	No adverse tissue reaction after two and six weeks. Photographs on file.

Human tests on the product of Example 1 are underway. The most notable ones are at the University of Missouri at Kansas City, Mo., one involving twenty patients in an 18 month controlled study; the other 20 patients over 12 months. Periodic recalls and reexaminations are ongoing in each study. Results so far are satisfactory.

As those of ordinary skill in the art will readily understand, a number of variations and adjustments are possible within the scope of this invention. It is accordingly not intended to limit the scope of the invention described unless the appended claims so require.

What is claimed is:

1. A biologically compatible non-toxic composition suitable, when mixed, as an in situ curing endodontic filling material which comprises two separately packaged components as follows:

(a) a paste component comprising a low viscosity hydroxy terminated polydialkylsiloxane and a non-reactive hydroxy-free silicone oil diluent having a viscosity of from about 20 to 20,000 centistokes at 25° C. and comprising a polydialkylsiloxane; and

(b) a liquid component comprising (i) the reaction product obtained by refluxing at ambient pressure and a temperature of about 150° to about 175° C. under a nitrogen blanket in the absence of air and moisture (1) a dialkyltindicarboxylate in which the alkyl groups have from 1 to about 8 carbon atoms and the carboxylate groups contain from about 10 to about 18 carbon atoms and (2) a tetraalkyl orthosilicate, in the molar ratio of 1 to 3; (ii) uncombined alkyl orthosilicate and (iii) a non-reactive hydroxy-free silicone oil diluent having a viscosity of from about 20 to 120,000 centistokes at 25° C. and comprising a polydialkylsiloxane.

2. The material of claim 1 in which component (a) comprises about 20 to 70% by weight of hydroxy terminated polydialkylsiloxane and up to about 70% by weight based on the hydroxy terminated polydialkylsiloxane of silicone oil diluent and component (b) comprises about 5 to 30% by weight of said reaction product, about 40 to 60% by weight tetraalkyl orthosilicate and about 15 to 45% by weight silicone oil diluent.

3. The material of claim 2 in which component (a) comprises about 25 to 50% by weight of hydroxy terminated polydialkylsiloxane and about 50 to 70% by weight based on the hydroxy terminated polydialkylsiloxane of silicone oil diluent and component (b) comprises about 10 to 15% by weight of said reaction product, about 50 to 55% by weight tetraalkyl orthosilicate and about 30 to 35% by weight silicone oil diluent.

4. The material of claim 2 in which component (a) also contains at least one pigment and an X-ray opaquing agent.

5. The material of claim 4 in which the X-ray opaquing agent is barium sulfate.

6. The material of claim 4 in which zinc oxide is present as a pigment.

7. The material of claim 6 in which red iron oxide is also present as a pigment.

8. The material of claim 2 in which titanium dioxide is present as a pigment, and component (a) contains no silicone oil diluent.

9. The material of claim 8 containing an alkanoic acid of 8–12 carbon atoms as a retarder of initial setting of the total composition after mixing.

10. The material of claim 9 in which the alkanoic acid is neodecanoic acid.

11. The material of claim 10 in which red iron oxide is also present as a pigment.

12. The material of claim 1 packaged in kit form with component (a) in a compressible tube-type container and component (b) in a sealed bottle.

* * * * *

United States Patent [19]

McLean et al.

[11] Patent Number: 4,527,979

[45] Date of Patent: Jul. 9, 1985

D3

83

43

[54] POWDERED DENTAL MATERIAL AND PROCESS FOR THE PREPARATION THEREOF

[75] Inventors: John W. McLean, London, England; Oswald Gasser, Seefeld, Fed. Rep. of Germany

[73] Assignee: ESPE, Fabrik pharmazeutischer Präparate GmbH, Seefeld, Fed. Rep. of Germany

[21] Appl. No.: 563,749

[22] Filed: Dec. 21, 1983

[30] Foreign Application Priority Data

Dec. 28, 1982 [DE] Fed. Rep. of Germany 3248357

[51] Int. Cl.³ A61K 6/08

[52] U.S. Cl. 433/228; 106/35; 260/998.11; 433/9; 433/226; 523/115; 523/116; 523/117; 523/118

[58] Field of Search 260/998.11; 106/35; 523/115, 116, 117, 118; 433/228, 9, 226

[56] References Cited

U.S. PATENT DOCUMENTS

3,814,717 6/1974 Wilson 260/998.11

4,209,434 6/1980 Wilson et al. 106/35

4,376,835 3/1983 Schmitt et al. 106/35

FOREIGN PATENT DOCUMENTS

2028835 3/1980 United Kingdom .

Primary Examiner—Lorenzo B. Hayes

Attorney, Agent, or Firm—Birch, Stewart, Kolasch & Birch

[57] ABSTRACT

Powdered dental material of a sintered mixture of calcium aluminum fluorosilicate glass and precious metals (or alloys thereof with each other or with up to 40% non-precious metals), which may optionally contain polycarboxylic acid and/or a chelating agent and/or further powdered precious metal. The dental material can be prepared by sintering a mixture of the glass and the precious metal at a temperature greater than 600° C., grinding the sintered product to a powder and admixing the optional further components. Use of the self-hardening glass ionomer cements for dental filling purposes gives fillings having excellent resistance to wear, most notably at the edges and corners in the molar region.

19 Claims, No Drawings

POWDERED DENTAL MATERIAL AND PROCESS FOR THE PREPARATION THEREOF

The invention relates to a powdered dental material, its preparation and its use.

Glass ionomer cements constituting the reaction product of a calcium aluminum fluorosilicate glass powder, a water-soluble polycarboxylic acid and water offer the advantage over other dental materials used for filling purposes (e.g., composite plastic fillings and amalgams) of being biologically compatible and of chemically bonding to the tooth substance so that they provide a perfect marginal seal. The disadvantage of the glass ionomer cements resides in their relatively high brittleness which has hitherto precluded the use thereof in the molar region and at corners and edges.

Metal-containing glass ionomer cement powders are disclosed in British Pat. No. 2,028,855. However, these are mere mixtures of cement powder and metal powder which have not been subjected to thermal treatment. The wear resistance of these mixtures tends to be inferior to that of pure glass ionomer cements.

West German patent application (OLS) No. 30 42 008, laid open for public inspection, teaches a tooth filling material which consists of a matrix-like metallic component with open voids and a non-metallic component, e.g., a glass ionomer cement, as a liquid or plastic material. For the production thereof the matrix-like metallic component is either wetted or impregnated with the non-metallic component, or the matrix-like metallic component is kneaded into the non-metallic component. The matrix-like metallic component may be produced by sintering metal powders. In this tooth filling material also, the metallic component is only mixed, for example, with the glass ionomer cement without having been previously sintered with a calcium aluminum fluorosilicate glass.

It is an object of the present invention to provide a powdered dental material on the basis of a glass ionomer cement powder which exhibits better wear resistance than that of a pure glass ionomer cement.

According to the invention, this object is realized by the provision of a powdered dental material comprising (a) calcium aluminum fluorosilicate glass, (b) precious metals customarily used for dental purposes or the alloys thereof with one another and/or with up to 40% by weight of non-precious metals, based on the weight of the alloy, and, optionally, (c) at least one dry polycarboxylic acid and/or chelating agent, which contains at least a portion of the component (a) in the form of a sintered mixture with the component (b).

According to the invention, the novel powdered dental material is produced by mixing a powder of (a) calcium aluminum fluorosilicate glass and (b) of precious metals customarily used for dental purposes such as gold or silver or the alloys thereof with one another and/or with up to 40% by weight of non-precious metals, based on the weight of the alloy, sintering the resulting mixture at a temperature in excess of 600° C., optionally after molding it into a shaped structure, and grinding the sintered product to form a powder. The resulting sintered product may optionally be blended with (1) unsintered calcium aluminum fluorosilicate glass and/or (2) with dry polycarboxylic acid and/or (3) with a chelating agent, each in powdered form.

For use, the powdered dental material of the invention, in case (1), is mixed with an aqueous polycarboxylic acid solution optionally containing a chelating agent; in case (2) it is mixed with water optionally containing a chelating agent, e.g., tartaric acid; and in case (3) it is mixed with aqueous polycarboxylic acid or with water to form a tooth filling material which exhibits high resistance to wear so that it is suited also for forming edges and corners in the molar region. The cement prepared from the dental material of the invention adheres to the tooth substance and is physiologically and biologically compatible.

Calcium aluminum fluorosilicate glass powders useful for the dental material of the invention have been described in, for example, U.S. Pat. Nos. 3,814,717 and 4,376,835.

The calcium aluminum fluorosilicate glass powders employed according to the invention preferably consist of the following components, in addition to oxygen:

Component	Calculated as	% by Weight
Si	SiO_2	20 to 60
Al	Al_2O_3	10 to 50
Ca	CaO	1 to 40
F	F	1 to 60
Na	Na_2O	0 to 10
P	P_2O_5	0 to 10

and altogether 0 to 20% by weight, calculated as oxides, of B, Bi, Zn, Mg, Sn, Ti, Zr, La or other trivalent elements of the lanthanide series, K, W, Ge and further additives which do not impair the properties thereof and which are biologically unobjectionable.

Preferably the powder particles consist of

Si as SiO_2	25 to 50% by weight
Al as Al_2O_3	10 to 40% by weight
Ca as CaO	10 to 35% by weight
F	5 to 50% by weight
Na as Na_2O	0 to 5% by weight
P as P_2O_5	1 to 10% by weight

and 0 and 10% by weight of B_2O_3, Bi_2O_3, ZnO, MgO, SnO_2, TiO_2, ZrO_2, La_2O_3 or other oxides of trivalent elements of the lanthanide series, K_2O, WO_3, GeO_2 and further additives which do not impair the properties thereof and which are biologically unobjectionable.

Especially preferred powders contain

Si as SiO_2	25 to 45% by weight
Al as Al_2O_3	20 to 40% by weight
Ca as CaO	10 to 30% by weight
F	10 to 30% by weight
Na as Na_2O	1 to 5% by weight
P as P_2O_5	1 to 10% by weight

Examples of the preferably used compositions are compiled in the following Table I.

TABLE I

	Percent by Weight			
	A	B	C	D
Si as SiO_2	19.0	17.6	29.0	45.4
Al as Al_2O_3	30.4	26.0	25.1	13.0
Ca as CaO	14.9	23.5	24.6	10.1
F	17.7	17.0	23.0	10.4
Na as Na_2O	2.7	2.1	2.2	6.9
P as P_2O_5	6.9	8.3	5.8	2.4

The glass powder particles used according to the invention may be depleted in calcium at the surface so that the quotient of the atomic ratio Si/Ca at the powder particle surface and the atomic ratio Si/Ca in the core region is at least 2.0, preferably at least 3.0, and most preferably at least 4.0 (see U.S. Pat. No. 4,376,835). These powders are used especially advantageously as an admixture to the ground metal-containing sintered product.

The glass powders employed according to the invention have an average particle size (weight average) of at least 1 micron and preferably at least 3 microns. The average particle size (weight average) ranges from 1 to 20 microns, preferably 3 to 15 microns, and most preferably 3 to 10 microns. The particles have a maximum particle size of 150 microns, preferably 100 microns, especially 60 microns. For use as a fixing cement, the maximum particle size is 25 microns, preferably 20 microns. In order to obtain good mechanical properties it is favorable to have a particle size distribution that is not too narrow, as usual, and which is attained, for example, by conventional grinding and screening off of coarser fractions.

As usual, the glass powders are obtained by co-melting the starting components at temperatures above 950° C., quenching and grinding. The compounds disclosed, for example, in U.S. Pat. No. 3,814,717 may be employed in suitable quantitative ranges as the starting materials.

The thus obtained powders are then optionally subjected to a surface treatment as described in U.S. Pat. No. 4,376,835. To this end the glass powders are subjected to a surface treatment with acid, preferably at room temperature. For this treatment substances containing acidic groups are employed, e.g., hydrochloric acid, sulfuric acid, nitric acid, acetic acid, propionic acid or perchloric acid, which form soluble calcium salts. The acids are used at a concentration from 0.01 to 10% by weight, preferably from 0.05 to 3% by weight.

After an adequate reaction period the powders are separated from the solution and thoroughly rinsed so that substantially no soluble calcium salts remain on the surface of the powder particles. The powder particles depleted in calcium on the surface are especially well suited for admixture with the ground metal-containing sintered products.

For use as precious metal powder, the precious metals customarily known and used in dentistry such as gold, platinum, palladium and silver are suitable, as well as the alloys thereof with one another and with up to 40% by weight of non-precious metals, based on the alloy weight, such as copper, tin, indium, and zinc. An example of an alloy useful in the present invention is an alloy composed of 65% by weight of silver and 35% by weight of tin. Silver and gold are the preferred precious metals, as well as the alloys thereof with not more than 10% by weight of other metals.

The average particle size (weight average) of the precious metal powder component (b) is at least 0.5 micron, preferably at least 1 micron, and most preferably at least 3 microns. Th weight average of the particle size distribution is preferably between 0.5 and 20 microns, especially between 1 and 10 microns. The maximum particle size of the metal powders should not exceed 60 microns, preferably 40 microns, and especially 10 microns. Preferably at least 90% of the particles of the precious metal powder component (b) have a particle size less than 32 microns, most preferably less than 10 microns.

The powdered dental material of the invention may also contain dry polycarboxylic acid. For this purpose, the polycarboxylic acids known for the production of glass ionomer cement powders may be employed, e.g., polymaleic acid, polyacrylic acid and mixtures thereof, or copolymers, especially maleic acid/acrylic acid copolymers and/or acrylic acid/itaconic acid copolymers.

Moreover, the dental material of the invention may contain a chelating agent (cf. U.S. Pat. No. 4,209,434). The preferred chelating agent is tartaric acid.

In order to carry out the process of the invention, first the powdered glass component (a) and the powdered precious metal component (b) are mixed. The proportion of the precious metal component (b) in the mixture of (a) and (b) may range from 20 to 80, preferably from 40 to 60% by volume of the mixture of (a)+(b).

The glass/metal powder mixture may be sintered directly. Thus, for instance, moldings may be produced in a pelletizer. Pelletizing is preferably carried out at high pressures, e.g., in a hydraulic press, especially at pressures above 3000 kg/cm². It is favorable to evacuate the pelleting chamber during the pelletizing operation, e.g., to a pressure of less than 10 mbar.

The powder mixture or the pellets made therefrom are sintered at temperatures above 600° C. Sintering preferably is effected in a vacuum, especially below 10 mbar, and most preferably below 5 mbar. The sintering temperature is maintained preferably below the melting point of the precious metal component (b) employed; if the precious metal component consists of silver or gold, a sintering temperature of about 800° C. is suitably employed. The sintering period may range from a few minutes to several hours, for example, from 10 minutes to 3 hours for pellets, depending on the size thereof. Before the sintered product is removed from the annealing furnace, it is favorable to allow it to cool to a temperature below 600° C.

The resulting sintered structures are ground to a fine powder in the usual way. The average particle size (weight average) and the maximum particle size of the powdered dental material are the same as those described above for the calcium aluminum fluorosilicate powder to be subjected to sintering.

The resulting powder may also be mixed with the above described unsintered calcium aluminum fluorosilicate glass powder. Preferably 10 to 50% by volume of unsintered calcium aluminum fluorosilicate glass powder are added, based on the sintered product. Powders depleted in calcium on the surface are especially suited for this purpose.

The ground sintered product or the mixture thereof with unsintered glass powder may also be mixed with dry, finely particulate polycarboxylic acid at a weight ratio of 1:1 to 5:1. Moreover, a chelating agent in powdered form may be added to any one of these mixtures.

The powdered dental materials of the invention are used in the manner customary for glass ionomer cement powders. In case the dental material of the invention does not contain dry polycarboxylic acid, it is mixed at a weight ratio from 2:1 to 10:1, preferably 4:1 to 8:1, with an aqueous polycarboxylic acid solution in which optionally a chelating agent, e.g., tartaric acid, is dissolved. For this purpose the same polycarboxylic acids, in the form of their aqueous solutions, as those which may be mixed in finely divided dry form with the metal-

containing powder of the invention are suitably employed. If the dental material of the invention already contains dry polycarboxylic acid, the dental material is mixed with water, optionally with the addition of a chelating agent, to acquire a cement-like consistency.

Tooth filling cements prepared with the powdered dental material of the invention give tooth fillings which have excellent resistance to wear, notably at the edges and corners in the molar region, while tooth fillings of glass ionomer cements without metal content or merely with admixed metal content are subject to relatively rapid decay due to edge breakage and high abrasion.

In addition to filling purposes in the molar region, the dental materials of the invention may be used also for the usual fillings if they are not in the directly visible area of the teeth. Furthermore, the material of the invention can be used for building up destroyed stumps prior to crowning. If the maximum particle size of the material does not exceed 20 microns, the dental material of the invention is suited also for use as fixing cement, e.g., for crowns and bridges.

Primarily with the use of gray metals, such as silver, the color of the filling material can be improved by the addition of up to 5% of a white or yellow pigment (e.g., titanium dioxide or zinc oxide). In this way, the material is also suitable for filling purposes in the front region on the lingual side of the teeth.

The following Examples are given merely as illustrative of the present invention and are not to be considered as limiting.

EXAMPLE 1

Gold-Containing Sintered Powder

A calcium aluminum fluorosilicate glass powder of the composition A in Table I (average particle size, 8 microns) is intimately blended at a volume ratio of 1:1 with a fine gold powder (99% gold, all particles smaller than 5 microns) and molded into cylindrical pellets of 13 mm diameter and 5 mm height at a pressure of 7000 kg/cm² under a vacuum of 4 mbar.

The pellets are heated in a vacuum of 4 mbar and at a temperature of 800° C. for 1 hour. After the furnace has cooled down to a temperature below 600° C., the pellets are removed and ground in a ball mill. Thereafter, particles of 40 microns and larger are screened off.

The resulting powder is mixed at a volume ratio of 4:1 with the above described unsintered calcium aluminum fluorosilicate glass powder previously depleted in calcium at the surface by treatment with 0.1% hydrochloric acid, as described in U.S. Pat. No. 4,376,835.

The resulting dental material is mixed at a weight ratio of 3:1 with a solution of 37 grams of a copolymer (1:1) of acrylic acid and maleic acid, 9 grams of tartaric acid and 54 grams of water. The thereby obtained cement mixture can be processed within about 3 minutes and hardens in about 8 minutes.

A molar filling made from this cement has a glossy golden surface; after having been in the mouth for 3 years it does not show any visible wear. Surface gloss and color have even slightly improved as compared with the initial state.

EXAMPLE 2

Silver-Containing Sintered Powder

17.5 parts by weight of calcium aluminum fluorosilicate glass powder corresponding to the composition B in Table I (average particle size, 5 microns) are homogeneously blended with 82.5 parts by weight of a finely divided silver powder (silver powder II F of Messrs. Degussa, average particle size 3.5 microns, 99.9% Ag) and processed as described in Example 1 by molding, sintering, grinding and mixing with the same untreated calcium aluminum fluorosilicate glass powder to form a powdered dental material.

After processing as described in Example 1, tooth fillings are made in the molar region. The fillings have a metallic gray gloss which has darkened only slightly after an observation period of 2 years; the fillings do not show any wear.

Comparative Test

In several test persons, fillings were placed in the molar region which were based on the following cement powders:

(a) gold-containing dental material of the invention as described in Example 1;
(b) silver-containing dental material of the invention as described in Example 2;
(c) glass ionomer cement powder according to Example 1 of U.S. Pat. No. 4,376,835;
(d) a powder composed according to (a) which, however, had not been subjected to a sintering treatment.

After two years in the test persons' mouths, the fillings were examined and showed the following results:

(a) intact glossy golden surface, no visible wear;
(b) intact glossy, slightly darker surface, no visible wear;
(c) slightly rough surface, defects by breakage in the edge regions,
(d) rough surface with visible abrasion, breakage in the edge regions.

From these results, it is clear that the dental material of the present invention provides improved results over glass ionomer cement powders which have not been sintered or subjected to a thermal treatment.

The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be considered as a departure from the spirit and scope of the invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the following claims.

We claim:

1. A powdered dental material composition comprising (a) calcium aluminum fluorosilicate glass and (b) a member selected from the group consisting of precious metals suitable for dental use and alloys of said precious metals with one another and/or with up to 40% by weight of non-precious metals, based on the weight of the alloy, at least a portion of the component (a) being in the form of a sintered mixture with the component (b).

2. A powdered dental material composition according to claim 1, further including a polycarboxylic acid and/or a chelating agent, each in powdered form.

3. A powdered dental material composition according to claim 1, wherein unsintered calcium aluminum fluorosilicate glass powder depleted in calcium at the surface thereof, the quotient of the atomic ratio Si/Ca at the powder particle surface and the atomic ratio Si/Ca in the core region being at least 2.0, is present in admixture with the powdered metal-containing sintered dental material.

4. A powdered dental material composition according to claim 3, wherein said quotient is at least 3.0.

5. A powdered dental material composition according to claim 1, wherein the average weight average particle size ranges from 1 to 20 microns.

6. A powdered dental material composition according to claim 5, wherein the average weight average particle size ranges from 3 to 10 microns.

7. A powdered dental material composition according to claim 1, wherein the precious metal is gold, platinum, palladium or silver.

8. A powdered dental material composition according to claim 7, wherein the non-precious metal is copper, tin, indium or zinc.

9. A powdered dental material composition according to claim 2, wherein the polycarboxylic acid is polymaleic acid, polyacrylic acid, maleic acid/acrylic acid copolymers, acrylic acid/itaconic acid copolymers or mixtures thereof.

10. A powdered dental material composition according to claim 2, wherein the chelating agent is tartaric acid.

11. A process for preparing a powdered dental material composition according to claim 1 which comprises mixing a powder of (a) calcium aluminum fluorosilicate glass and (b) a member selected from the group consisting of precious metals suitable for dental use and alloys of said precious metals with one another and/or with up to 40% by weight of non-precious metals, based on the weight of the alloy, sintering the resulting mixture at a temperature in excess of 600° C., and grinding the sintered product to form a powder.

12. A process according to claim 11, wherein the mixture of component (a) and component (b) is molded into a shaped structure prior to sintering.

13. A process according to claim 11, wherein the sintered powder is mixed with unsintered calcium aluminum fluorosilicate glass, at least one polycarboxylic acid and/or a chelating agent, each in powdered form.

14. A process according to claim 11, wherein the proportion of component (b) is from 20% to 80% by volume of the mixture of components (a) and (b).

15. A process according to claim 11, wherein the sintering is carried out in a vacuum of less than 10 mbar.

16. A process according to claim 11, wherein the precious metal is silver or gold and the sintering is carried out at a temperature less than the melting point thereof.

17. A process according to claim 13, wherein unsintered calcium aluminum fluorosilicate glass powder is mixed with the sintered powder, said unsintered glass powder being depleted in calcium at the surface thereof, the quotient of the atomic ratio Si/Ca at the powder particle surface and the atomic ratio Si/Ca in the core region being at least 2.0.

18. A self-hardening glass ionomer dental cement or filling material comprising the dental material composition of claim 2 and water.

19. A method of filling teeth or for cementing dental crowns and bridges which comprises applying the glass ionomer dental filling material or cement of claim 18 as the filling material or fixing cement to the teeth to be treated.

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES

2020
Bogotá, D.C., 26/09/2008

Abogado
Dilia Rodríguez D'Alemán
(Apoderado)

ASUNTO	Radicación	05 123306
	Trámite	002
	Evento	001
	Actuación	430
	Oficio	- 12278
	Folios	006

Patente de Invención [X] Patente de Modelo de Utilidad [ ]

Vía Nacional [ ]

Vía PCT (fase nacional) [X] Cap. I [ ] Cap. II [X]

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica:

1. Documentos estudiados

1.1. Descripción: Folios: 20 a 41

1.2. Reivindicaciones: Folios: 42 a 44

1.3. Datos PCT:

Solicitud Internacional:	PCT/NL2004/000396
Capítulo II	
Fecha Sol. Internacional:	03/06/2004
Publicación. Internacional:	WO04/108095
Fecha Pub. Internacional:	16/12/2004
Fecha Inicio Fase Nacional:	05/01/2006
Fecha Sol. Nacional:	05/12/2005

1.4. Prioridad: EP03076770.1 de 05/06/2003
US60/475.903 de 05/06/2003

2. Objeto de la invención

Título de la solicitud

Composición de carbómero de vidrio de autoendurecimiento

Reivindicaciones

Reivindicaciones 1 a 8: Se reivindica una composición de carbómero de vidrio de autoendurecido obtenible al tratar un polvo de vidrio con fluorosilicato con:

a) Un poli(dialquisiloxano) que tiene grupos hidroxilo terminales y que puede ser lineal o cíclico, en donde los grupos alquilo contienen 1 a 4 átomos de carbono y son preferiblemente metilo.
b) Una solución de ácido acuoso que puede ser de un ácido orgánico como un polímero o un ácido inorgánico y se encuentra en un rango de pH entre 2 y 7.
c) Separar el polvo de vidrio con fluorosilicato tratado con la solución de ácido acuoso

La composición de carbómero de vidrio de autoendurecido se caracteriza porque el poli(dialquilsiloxano) tiene una viscosidad cinemática de 1 a 100.000 Cst a 25°C y las partículas de polvo de vidrio de fluorosilicato tiene un tamaño promedio de cerca de 0.5 a cerca de 200µm.

Reivindicación 9: Se reivindica el proceso para preparar una composición de carbómero de vidrio de fluorosilicato que consiste en:

a) Un poli(dialquisiloxano) que tiene grupos hidroxilo terminal y que puede ser lineal o cíclico, en donde los grupos alquilo contienen 1 a 4 átomos de carbono
b) Una solución de ácido acuoso
c) Separar el polvo de vidrio con fluorosilicato tratado con la solución de ácido acuoso

Reivindicación 10: Se reivindican el uso del carbómero de vidrio de autoendurecido como un material de relleno dental, un cemento de pegado dental, un cemento óseo o un material de reemplazo óseo.

Sustento Descriptivo

La invención se relaciona con un cemento de carbómero de vidrio que tiene propiedades mejoradas, un método para preparar dicho cemento de carbómero de vidrio y el uso de dicho cemento de carbómero de vidrio en aplicaciones clínicas y dentales que incluyan aplicaciones de alta tensión, por ejemplo, restauración de dientes, reemplazo de dentina, incrustaciones de núcleos de corona, es decir, como hueso y cemento dental, y aplicaciones industriales.

El objetivo de la invención es suministrar una composición de ionómero de vidrio que cuando se endurece tienen propiedades mejoradas con respecto a los ionómeros de vidrio conocidos en la técnica. Las composiciones de carbómero de vidrio de acuerdo con la invención tienen buena dureza y tensión y excelente liberación de fluoruro, no muestran contracción o expansión y esta característica resulta esencial para suministrar relleno en las cavidades que tienen alta tensión y requieren larga durabilidad.

- Una vez catalogada la invención ésta se clasificó en la sección: **A 61 K $^{6}/_{06}$ // $^{6}/_{093}$ de la Clasificación Internacional de Patentes.**

3. Reivindicaciones relativas a un uso *(artículos 14 D. 486)*

La cláusula 10 que hace referencia al uso del carbómero de vidrio de autoendurecido contempla un objeto que no es susceptible de protección. Al respecto es preciso señalar que mediante dicha cláusula la solicitud incorpora una categoría de invención que no ha sido contemplada por el ordenamiento jurídico andino.

La Decisión 486 define de manera taxativa el grupo de invenciones susceptibles de protección a través del privilegio de patente y precisa que sólo los productos y procedimientos en los diversos campos tecnológicos pueden ser objeto del título, motivo por el cual, resulta procedente requerir al señor solicitante en los términos del presente examen técnico para que elimine del alcance de su invención la cláusula en comento.

4. Determinación del Estado de la Técnica

Considerando que la fecha de presentación de la primera solicitud de patente de la cual se reivindica prioridad es: 05/06/2003, se procedió a efectuar la búsqueda de documentos relacionados en el estado de la técnica con fecha de publicación anterior a ésta.

N°	Documento	Título	Fecha de Publicación
D1	US4376835	"Calcium depleted aluminum fluorosilicate glass powder for use in dental or bone cements"	15/03/1983
D2	US4449938	"Endodontic filling and sealing composition"	22/05/1984
D3	US4527978	"Powdered dental material and process for the preparation thereof"	09/07/1985

Anterioridades D1 a D3 en los folios 70 a 87

5. Análisis de patentabilidad (*artículo 14 D. 486*)

5.1 Nivel inventivo *(artículo18 D. 486)*

El nivel inventivo del objeto reclamado se evaluó por comparación entre las características esenciales de las estructuras definidas en el pliego reivindicatorio y los elementos esenciales revelados por el arte previo.

- **Se reivindica una composición de carbómero de vidrio de autoendurecido obtenible al tratar un polvo de vidrio con fluorosilicato con:**

  a) Un poli(dialquisiloxano) que tiene grupos hidroxilo terminales y que puede ser lineal o cíclico, en donde los grupos alquilo contienen 1 a 4 átomos de carbono y son preferiblemente metilo.
  b) Una solución de ácido acuoso que puede ser de un ácido orgánico como un polímero o un ácido inorgánico y se encuentra en un rango de pH entre 2 y 7.
  c) Separar el polvo de vidrio con fluorosilicato tratado con la solución de ácido acuoso

La composición de carbómero de vidrio de autoendurecido se caracteriza porque el poli(dialquilsiloxano) tiene una viscosidad cinemática de 1 a 100.000 Cst a 25°C y las partículas de polvo de vidrio de fluorosilicato tiene un tamaño promedio de cerca de 0.5 a cerca de 200µm.

- **El estado del arte previo a la invención presenta los siguientes documentos:**

Anterioridad D1:
La publicación **D1** revela composiciones de polvo de vidrio calcio-alumino-fluorosilicato de tamaño de partícula de 0,5µm, que se caracteriza porque el calcio se encuentra en la superficie de las partículas de polvo y se encuentra depletado en un coeficiente de radio atómico Si/Ca tanto en la superficie y en el centro de las partículas que fluctúa entre 2.0, 3.0 y 4.0.

El polvo puede ser preparado mediante un proceso que consiste en las siguientes etapas:

a) Tratar las partículas de polvo de vidrio calcio-alumino-fluorosilicato que presentan un tamaño de al menos 0,5µm y un tamaño máximo de 150µ con una solución acuosa de un ácido que tiene una concentración de 0.01 a 10% p/p.
b) Separar el polvo tratado de la solución ácida y,
c) secar el polvo lavado. El polvo puede ser empleado para asegurar y endurecer el cemento de vidrio ionómero que se utiliza comúnmente para huesos o cementos dentales.

Anterioridad D2:
La publicación **D2** revela materiales que se componen de **a)** un 20 a 70% en peso de un polidialquilsiloxano que tiene grupos hidroxilo terminales y que contiene por encima del 70% un polidialquilsiloxano con aceite de silicona como diluente y **b)** del 5 al 30% del producto de la reacción y del 40 al 60% en peso de tetraalquil ortosilicato y cerca del 15 al 45% en peso del diluente aceite de silicona.

Anterioridad D3:
La publicación **D3** revela materiales para uso dental que contienen polvo de vidrio de calcio-alumino-fluorosilicato como cemento ionomérico y opcionalmente puede utilizar un ácido policarboxílico y un agente quelante y/o materiales o piedras preciosas.

Dicho material se usa porque presenta dureza y resistencia suficiente en los bordes y coronas en la región de los molares.

La reivindicación 3 del antecedente **D3** indica que en los intersticios y en la superficie del polvo de vidrio de fluorosilicato se depleta calcio en un cociente Si/Ca que tiene un radio atómico de 2 (ver folio 66 columna 6 líneas 61 a 68.

Al evaluar los elementos característicos de la invención y compararlos con las enseñanzas de los antecedentes más próximos **D1** y **D2** es posible concluir lo siguiente:

La diferencia entre la materia reivindicada y la publicación **D1** estriba en que el documento de la publicación **D1** no indica la adición de fluoro silicato para la obtención del copolímero, sin embargo indica paso a paso las etapas que fueron objeto de reivindicación por parte del señor solicitante.

Con respecto al documento **D2** se identifica que el material polimérico obtenido es un copolímero formado entre polidialquilsiloxano (PDMS) y un silicato que es de tipo tetra-alquil-orto silicato, mientras que el señor solicitante indica que la composición del polímero obtenido según las cláusulas 1 a 8 es de polidialquilsiloxano con calcio-alumino-fluorosilicato.

En este orden de ideas es posible concluir que si bien existen diferencias técnicas entre los antecedentes **D1** y **D2** y la materia reivindicada, al combinar las enseñanzas de los documentos es posible derivar un producto como el que se reivindica a través de su proceso de obtención, dado el mismo documento **D2** indica que dicho material tiene propiedades tixotrópicas y puede permanecer por largos periodos en la superficie dental porque es de curado apresurado.

Ahora bien, el documento **D3** expone las propiedades del polvo de vidrio fluorosilicato e indica que se utiliza como cemento ionómero con los iones calcio y aluminio para el propósito de la fabricación de amalgamas. En dicho documento el investigador indica que su combinación con otros materiales le otorga mayor dureza además que resulta fisiológica y biológicamente compatible.

En dicho documento combinan el calcio-alumino-fluorosilicato con metales preciosos como oro y plata, sin embargo, al combinar sus enseñanzas con las del documento **D2** que publica los resultados superiores alcanzados cuando se combina polvo de vidrio tetra-alquil-ortosilicato con una sustancia polimérica de tipo silicona como el polidialquil-siloxano, es posible derivar tanto la composición reivindicada como el proceso para la obtención del copolímero.

Para esta Dependencia es claro que uno de los indicios de falta de nivel inventivo constituye el intercambio de material por uno análogo conocido así como el uso de equivalentes técnicos conocidos, de esta manera al combinar las enseñanzas de los documentos **D2** y **D3** es posible derivar las características técnicas del copolímero reivindicado.

Por otra parte, el proceso reclamado se encuentra ampliamente ilustrado en el documento **D1**, el cual al combinarse con el documento **D2** da cuenta de la obviedad y derivación a partir del estado del arte de las etapas del proceso que se reclaman en la cláusula 9 y de las que permiten definir la composición del material para uso como relleno dental.

De esta manera, la materia objeto de la presente solicitud se encuentra afectada por las enseñanzas del arte previo en particular en lo atinente al nivel inventivo, dado que la composición reclamada no constituye un verdadero salto en la regla técnica y no hay evidencia dentro del soporte descriptivo que demuestre el efecto inesperado de cambiar el agente tetra-alquil-orto silicato por fluorosilicato, máxime si se tiene en cuenta que el arte previo ya los catalogaba como sustancias con capacidad para formar materiales poliméricos tipo amalgama para el cuidado de los dientes.

En conclusión existe incumplimiento de las disposiciones normativas del artículo 18 de la Decisión 486.

6. Conclusión:

Los requisitos de patentabilidad de la presente solicitud se encuentran afectados así:

N°	Documento N°	Reivindicaciones Afectadas	Requisito que Afecta
D1	US4376836	1 a 10	Nivel Inventivo
D2	US449938	1 a 10	Nivel Inventivo
D3	US4527979	1 a 10	Nivel Inventivo

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta días contados a partir de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única N° 10 de 2001.

ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe de División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista, de fecha 03 OCT. 2008.

CONCEPTO TÉCNICO No. 2814	EXAMINADOR TÉCNICO Código No. 202044