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PATENT REQUEST: STANDARD PATENT

We, THERA PATENT GmbH & CO. KG, being the person(s) identified below as the Applicant, request the grant of a standard patent to the person identified below as the Nominated Person, for an invention described in the accompanying complete specification.

AUSTRALIAN PATENT OFFICE SEC. 113

Full application details follow.

Applicant: SECTION 113 DIRECTION SEE FOLIO 4

Address: NAME DIRECTED THERA PATENT-VERWALTUNGS-GMBH Griesberg 2, D-8031 Seefeld 1, Federal Republic of Germany

Nominated Person: Gesellschaft fur industrielle Schutzrechte

Address: GRIESBERG 2 D-8031 Seefeld 1 Federal Republic of Germany

Invention Title: "FORMABLE COMPOSITION AND ITS USE AS FILLING MATERIAL FOR DENTAL ROOT CANALS"

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Attorney Code: RI

BASIC CONVENTION APPLICATION(S) DETAILS

Application No.	Country	Country Code	Date of Application
P4024322.2	Federal Republic of Germany	DE	31 July 1990

We are not an eligible person described in Section 33 - 36 of the Act.

Dated this 29 day of July 1991

THERA PATENT GmbH & CO. KG

By: _____
Registered Patent Attorney

P0332AU 29/07/91

Commonwealth of Australia
The Patents Act 1952

DECLARATION IN SUPPORT

In support of the (Convention) Application made by: THERA PATENT GmbH & Co. KG of Griesberg 2, D-8031 Seefeld 1, Germany

for a patent for an invention entitled: Formable Composition and its Use as Filling Material for Dental Root Canals

~~I~~ (We) DR Oswald Gasser & Dr Reinhold Nowak

of and care of the applicant company do solemnly and sincerely declare as follows:

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a) ~~I am (We are) the applicant(s) for the patent~~
or
b) ~~I am~~ (We are) authorised by the applicant(~~s~~) for the patent to make this declaration on its behalf.

Delete the following if not a Convention Application.

The basic application(~~s~~) as defined by section 141 (~~142~~) of the Act was (~~were~~) made

on July 31, 1990 in Federal Republic of Germany (P 40 24 322.2)

on in

on in

by THERA Patent GmbH & Co. KG
Gesellschaft für industrielle Schutzrechte

The basic application(~~s~~) referred to in this paragraph is (~~are~~) the first application(~~s~~)-made in a Convention country in respect of the invention the subject of the application.

---

a) ~~I am (We are) the actual inventor(s) of the invention~~

or b) Dr. Oswald Gasser of Höhenstr. 10, D-8031 Seefeld, Federal Republic of Germany and
Dr. Rainer Guggenberger of Siglstr. 10, D-8036 Herrsching, Federal Republic of Germany

~~is~~ (are) the actual inventor(s) of the invention and the facts upon which the applicant

is (~~are~~) entitled to make the application are as follows:
The applicant is a person who would if a patent were granted upon application made by the actual inventors be entitled to have the patent assigned to it.

Declared at Seefeld this 26. day of June 19 91

Signed i.V. Dr. O. Gasser Status Executive secutary
Authorized agent

Declarant's Name Dr. Oswald Gasser Dr. Reinhold Nowak

F. B. RICE & CO PATENT ATTORNEYS

This form is suitable for any type of Patent Application. No legalisation required.

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FORMABLE COMPOSITION AND ITS USE AS FILLING MATERIAL FOR DENTAL ROOT CANALS

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(57) Claim

1. Formable composition comprising

(A) 25 to 80 wt-% of a glass ionomer cement, containing

(a) an aluminium fluorosilicate glass having an average particle size of 1 to 20μm, and a maximum particle size of 150μm,

(b) at least one polymeric polyacid with an average molecular weight 〉 500,

(c) 5 to 70 wt-% water relative to the total mass of (A), and

(d) optionally a chelate-forming agent and

(B) 20 to 75 wt-% of a fluoride and/or oxide and/or mixed fluoride and/or mixed oxide of heavy metal elements which is/are essentially insoluble in the aqueous polymeric polyacid and in the solution containing the chelating agent.

5. The formable composition according to claims 1 to 4, characterised in that the heavy metal element is a rare earth metal or a metal of the sixth sub-group of the periodic system.

6. The formable composition according to claims 1 to 5, characterised in that the component (B) is yttrium fluoride, zirconium dioxide, lanthanum oxide, calcium tungstate or strontium tungstate, preferably calcium tungstate.

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12. The formable composition according to claims 1 to 11, wherein the composition is used as filling material for dental root canals.

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~~THERA-PATENT-GmbH & CO. KG~~

ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT

Invention Title:

FORMABLE COMPOSITION AND ITS USE AS FILLING MATERIAL FOR DENTAL ROOT CANALS

The following statement is a full description of this invention including the best method of performing it known to us:-

Because of caries, loose fillings, traumatic processes and via other infection routes, the pulpa (i.e. the dental pulp) of the living tooth can become inflamed. In most cases this inflammation is irreversible so that the pulpa must be removed by the dentist. Apart from the pulpa, the bordering, infected hard tissue is also to be carefully removed, after which the cavity formed - the root canal - must once again be tightly sealed. To this end there is a number of products on the market which essentially comprise zinc oxide or calcium hydroxide together with an organic salt former. However, none of the materials completely meets the requirements of such a root canal filling material.

This material must tightly seal the canal in order to prevent the invasion by infectious germs - there is a danger of maxillary infection. A high degree of histocompatibility is to be required, because the cement can, upon emerging from the apex (dental root tip), come into contact with living tissue. Moreover, for maintaining tightness, the cement is to display only very slight solubility. Finally, for introduction into the narrow root canal, a sufficient processing time and a suitable viscosity are necessary.

In order to increase the tightness of the filling materials and to compensate for their shrinkage during the hardening reaction, the material is frequently used only as sealant together with

thin pegs made from gutta-percha (a filled, natural resin material). Following a text-book method, many such pegs are laterally condensed in the process, in order to keep the proportion of filling material as low as possible. However, this method is extremely time-consuming.

Glass ionomer cements are known for their tight edge-seal, because they display chemico-physical adhesion to the dental substance; furthermore, they show only very slight solubility and are categorized as histocompatible. However, they lack a sufficient processing time for introduction into the root canal. For the conventional application areas of glass ionomer cements - dental fillings, securing cements, sealant materials, stump reconstruction materials - the required processing time is only 2 - 3 minutes. For the filling of root canals including the necessary X-ray check, however, the dentist needs ca. 10 minutes. Furthermore, the viscosity of the glass ionomer cements is too high - i.e. the pastes are too solid - for them to be introduced into the root canal by conventional means. Diluting the system, however, leads to much too high a solubility.

Known from US patent specification 4 861 808 are glass ionomer compositions which contain a light metal fluoride, namely strontium fluoride, in order to make dental fillings made from these compositions X-ray visible. The X-ray opacity and the processibility of these known compositions are, however, not satisfactory.

US patent specification Re. 33 100 describes glass ionomer compositions which, to prevent irritation of the dental pulp, are

buffered with 5 to 20 wt-% of a soluble heavy metal oxide, namely zinc oxide, and 0 to 10 wt-% titanium dioxide. The processibility of these compositions and the durability of dental fillings made from these compositions are not satisfactory.

The aim of the invention is to make available a root canal filling material which meets the clinical requirements as ideally as possible, i.e. displays sufficient processing time and provides tight fillings which display high mechanical strength and slight solubility.

Surprisingly, it was ascertained that a suitable root canal filling material is obtained by adding certain heavy metal compounds to a conventional glass ionomer cement.

The invention relates to a formable composition comprising

(A) 25 to 80 wt-% of a glass ionomer cement, containing
  (a) an aluminium fluorosilicate glass,
  (b) at least one polymeric polyacid with an average molecular weight > 500,
  (c) water and
  (d) optionally a chelate-forming agent and

(B) 20 to 75 wt-% of a fluoride and/or oxide and/or mixed fluoride and/or mixed oxide of heavy metal elements essentially insoluble in the aqueous polymeric polyacid and in the solution containing the chelating agent.

Components (A) and (B) are preferably present in each case in quantities of 35 to 65 wt-%, particularly 50 to 65 wt-%.

Surprisingly, despite the high addition of inert heavy metal compound, i.e. despite clearly reducing the proprotion of reactive glass, relatively good mechanical strength and, above all, slight solubility are prisent, the mixture displaying a flowability which is well suited to the application. In addition, the processing time for the soft composition increases in the desired way without significant concessions with regard to solubility and mechanical strength.

The calcium aluminium flourosilicate glasses described in DE-A-20 61 513 and EP-A-0 023 013 and the strontium aluminium fluorosilicate glasses described in EP-A-O 241 277 can be used as constituent (A) (a). The aluminium fluorosilicate glass powders used according to the invention preferably consist of, in addition to oxygen:

Constituent	Calculated as	wt-%
Si	SiO_2	10-60
Al	Al_2O_3	10-50
Ca	Ca O	0-40
Sr	SrO	0-40
F	F	1-40
Na	Na_2O	0-10
P	P_2O_5	0-10

at least 1 wt-% and/or SrO having to be contained, and in total 0 to 30 wt-%, calculated as oxides, of B, Bi, ZN, Mg, Sn,

Ti, Zr, La or other trivalent lanthanoids, K, W, Ge as well as futher additives which do not impair the properties and are physiologically acceptable. The glasses can be made X-ray visible by adding 10 to 30 wt-% La_2O_3.

The powder particles advantageously consist of:

Si as SiO_2	20-50 wt-%
Al as Al_2O_3	10-40 wt-%
Ca as CaO	0-35 wt-%
Sr as SrO	0-35 wt-%
F	5-30 wt-%
Na as Na_2O	0-8 wt-%
P as P_2O_5	1-10 wt-%

Wherein 0-30 wt-% Ca (calculated as CaO) and/or Sr (calculated as SrO) are contained, and 0 - 10 wt-% of B_2O_3, Bi_2O_3, ZnO, MgO, SnO_2, TiO_2, La_2O_3 or other oxides of trivalent lanthanoids, K_2O, WO_3, GeO_2 as well as further additives which do not impair the properties and are physiologically acceptable.

Especially preferably used powders contain

Si as SiO_2	20-40 wt-%
Al as Al_2O_3	15-35 wt-%
Ca as CaO	5-25 wt-%
F	10-30 wt-%
Na as Na_2O	1-8 wt-%
P as P_2O_5	1-10 wt-%
La as La_2O_2	0-30 wt-%

The glass powders used according to the invention have an average particle size (weight average) of at least 1 µm and preferably at least 3 µm. The average particle size (weight average) is 1 - 20 µm, preferably 3 - 15 µm and especially preferably 3 - 10 µm. The particles have a maximum particle size of 150 µm, preferably 100 µm, especially 60 µm.

The resultant powders are then optionally subjected to a surface treatment as per European patent 0 023 013. To this end the glass powders are treated on the surface with acid, preferably at room temperature. Acid-group-containing substances are used, e.g. hydrochloric acid, sulphuric acid, nitric acid, acetic acid, propionic acid or perchloric acid, which form soluble calcium salts or strontium salts. The acids are used in a concentration of 0.01 to 10 wt-%, preferably of 0.05 to 3 wt-%. After the corresponding reaction time the powders are separated from the solution and thoroughly washed so that practically no more soluble calcium or strontium salts are located on the surface of the powder particles.

The polymeric polyacids to be used as constituent (A) (b) can also be the polycarboxylic acids known in the preparation of glass ionomer cement powders, e.g. polymaleic acid, polyacrylic acid, polyitaconic acid and mixtures thereof or copolymers, particularly the maleic acid/acrylic acid copolymers and/or acrylic acid/itaconic acid copolymers known from EP-A-0 024 056. The average molecular weight of the polycarboxylic acids to be used according to the invention is more than 500. An average molecular weight of 1,000 to 20,000 is advantageous, 3,000 to

10,000 being especially preferred. The polyacid is preferably used in concentrations of 5 to 50 wt-%, relative to constituent (A) (a).

Also suitable as polymeric polyacid are polyphosphonic acids, e.g. polyvinylphosphonic acid. These polyphosphonic acids can completely or partially replace the above-mentioned polycarboxylic acids.

Constituent (A) (c), water, is used in quantities of 5 to 70 wt-%, preferably 15 to 40 wt-%, relative to the total mass of (A).

A chelate-forming agent, such as is described in DE-A-23 19 715, can be contained as constituent (A) (d). Tartaric acid is preferably used as chelate-former. The chelate-formers can be used in concentrations of 0.1 to 10, preferably 3 to 8 wt-%, relative to the total mass of (A).

In order to obtain high storage-stability prior to application, it is advisable to add preservatives, e.g. benzoic acid, particularly to the dry polyacid.

Additives for regulating the viscosity (e.g. pyrogenic silicic acid) and for colouring (pigments) are possible. The viscosity regulators can be used in concentrations of 0.1 to 10, preferably 1 to 5 wt-%, relative to the total mass of (A).

The heavy metal compound present as component (B) is physiologically acceptable and inert, i.e. it is largely insoluble in the

10,000 being especially preferred. The polyacid is preferably used in concentrations of 5 to 50 wt-%, relative to constituent (A) (a).

Also suitable as polymeric polyacid are polyphosphonic acids, e.g. polyvinylphosphonic acid. These polyphosphonic acids can completely or partially replace the above-mentioned polycarboxylic acids.

Constituent (A) (c), water, is used in quantities of 5 to 70 wt-%, preferably 15 to 40 wt-%, relative to the total mass of (A).

A chelate-forming agent, such as is described in DE-A-23 19 715, can be contained as constituent (A) (d). Tartaric acid is preferably used as chelate-former. The chelate-formers can be used in concentrations of 0.1 to 10, preferably 3 to 8 wt-%, relative to the total mass of (A).

In order to obtain high storage-stability prior to application, it is advisable to add preservatives, e.g. benzoic acid, particularly to the dry polyacid.

Additives for regulating the viscosity (e.g. pyrogenic silicic acid) and for colouring (pigments) are possible. The viscosity regulators can be used in concentrations of 0.1 to 10, preferably 1 to 5 wt-%, relative to the total mass of (A).

The heavy metal compound present as component (B) is physiologically acceptable and inert, i.e. it is largely insoluble in the

polymeric polyacids usually used for glass ionomer cements, and it is chosen from the group of the fluorides and/or oxides and/or mixed oxides and/or mixed fluorides of heavy metal elements which are essentially insoluble in the aqueous polymeric polyacid and in the solution containing the chelating agent. Heavy metals are elements which display a density of ca. > 4. Preferred are oxides/fluorides of the rare earth metals and the sixth subgroup. Especially preferred is the group yttrium fluoride, zirconium dioxide, lanthanum oxide, calcium tungstate or strontium tungstate. Quite especially preferred is calcium tungstate. Optionally, the ~~The~~ average particle sizes are between 0.5 µm and 20 µm, preferably between 2 µm and 10 µm.

The composition according to the invention is preferably presented in a capsule which contains powder and fluid initially separated. After the powder and liquid have been brought together, the composition is prepared by mechanical mixing with a usual shaker device.

An application capsule according to EP-A-0 157 121 is preferably used, which especially preferably is provided with a small plastics tube as per DE-GM 90 03 983.1. With this, direct application of the mixed composition according to the invention into the root canal is possible.

The starting component (powder and liquid) is preferably provided sterile. The sterilization can take place by heat treatment, sterile filtration (liquid) or particularly by gamma radiation.

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The essential constituents of the glass ionomer cement

(A) (a) glass powder

(A) (b) polymeric polyacid

(A) (c) water

(A) (d) chelate-former

(B) heavy metal compound

can be divided in various ways:

Powder	Liquid
(A) (a) + B	- (A) (b) + (A) (c) + (A) (d)
(A) (a) + B + (A) (b)	- (A) (c) + (A) (d)
(A) (a) + B + (A) (b) + (A) (d)	- (A) (c)

Paste/paste divisions are also possible, in which e.g. combination with (A) (c) would be possible.

EXAMPLES

Example 1

A cement powder is prepared by intimate mixing of

- 75 g calcium tungstate
- 25 g calcium aluminium fluorosilicate glass of the following composition:

7 wt-% aluminium fluoride
13 wt-% aluminium oxide
12 wt-% aluminium phosphate
20 wt-% calcium fluoride
4 wt-% cryolite
20 wt-% lanthanum oxide
24 wt-% quartz

(average particle size 8 µm)
which had been treated for one hour with a 10-fold amount of 0.1 % hydrochloric acid, dried and heated for 6 hours at 400 °C.

- 4 g pyrogenic silicic acid and pigments.

In addition, a cement liquid was prepared by dissolving

35 g of a copolymer (1:1) comprising acrylic acid and maleic acid (average molecular weight ca. 8,000 Dalton) and

11.8 g tartaric acid in
53.2 g distilled water.

300 mg of the cement powder are homogeneously mixed, using a spatula, with
100 mg of the cement liquid.

The viscosity of the mixture is well suited for introducing the material into the root canal with the Lentulo (spiral-shaped introduction device). The X-ray check shows the filled-in cement to be homogeneous, edge-tight and void-free. The cement can be processed satisfactorily and shows good adhesion to the dental material. The physical data are given in Table 1.

Example 2

The calcium tungstate in the cement powder according to example 1 is replaced by 65 g zirconium dioxide (average particle size 6 µm).

Further processing is carried out as described in example 1. The cement obtained can be satisfactorily processed and introduced into the root canal (physical data see Table 1).

Example 3

100 mg of the liquid from example 1 are welded into a small film sachet and attached to an application capsule as per EP-A 0 157 121, the main chamber of which is filled with 300 mg of the

cement powder according to example 1. A small application tube according to DE-GM G 90 03 983.1 is attached to the tip of the movable nozzle. The capsule is welded into a blister film and sterilized with gamma rays. After mixing in a mechanical mixer (ESPE Capmix) (duration of mixing 10 seconds), the cement, which corresponds in its properties to the material according to example 1, can be directly applied into the root canal.

Comparative Example 1

A root canal filling material based on zinc oxide/propionyl/acetophenone (Diaket ®, ESPE), which is on the market, was mixed according to the manufacturer's instructions and processed (physical data see Table 1).

Comparative Example 2

A cement is prepared corresponding to example 1. Unlike this, however, the powder comprises only the described calcium aluminium fluorosilicate glass without the heavy metal compound according to the invention (see Table 1).

Table 1 - Physical Properties

	Example 1	Example 2	Comparative Example 1	Comparative Example 2
Processing time (23°C) [1]	11 min.	9:30 min.	10 min.	4 min.
Setting time (36 °C) [1]	10:30 min.	10 min.	135 min.	4:30 min.
Solubility [2]	0.4 %	0.6 %	0.5 %	0.3 %
Compressive strength [2]	90 MPa	82 MPa	<10 MPa	95 MPa
X-ray visibility [1]	9 mm Al	8 ml Al	5 mm Al	3 mm Al
Viscosity [1]	32 mm	33 mm	32 mm	25 mm

1) Measurement as per ADA No. 57
2) Measurement as per ISO 7489

By comparing the physical properties of the examples (Table 1), the following can be concluded:

The root filling materials according to the invention display a long processing time which cannot be achieved by a glass ionomer cement without additive (comparative example 2). The setting time is nevertheless relatively quick. It is considerably quicker than with root canal filling materials on the market (comparative example 1).

Despite the high content of inert heavy metal compound, solubility and compressive strength are virtually unchanged vis-à-vis a pure glass ionomer cement (comparative example 2). The compressive strength clearly lies above the current level of known root canal fillers (comparative example 1).

The viscosity of the compositions according to the invention is clearly improved vis-à-vis the pure glass ionomer cement. The improvement is of great importance for the practical application precisely because only an adequate flowability permits a homogeneous filling-in into the narrow root canal.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. Formable composition comprising

(A) 25 to 80 wt-% of a glass ionomer cement, containing

(a) an aluminium fluorosilicate glass having an average particle size of 1 to 20μm, and a maximum particle size of 150μm,

(b) at least one polymeric polyacid with an average molecular weight 〉 500,

(c) 5 to 70 wt-% water relative to the total mass of (A), and

(d) optionally a chelate-forming agent and

(B) 20 to 75 wt-% of a fluoride and/or oxide and/or mixed fluoride and/or mixed oxide of heavy metal elements which is/are essentially insoluble in the aqueous polymeric polyacid and in the solution containing the chelating agent.

2. The formable composition according to claim 1, characterised in that the component (A) is present in a quantity of 35 to 65 wt-%, and component (B) in a quantity of 35 to 65 wt-%.

3. The formable composition according to claim 2, wherein component (A) is present in a quantity of 50 to 65 wt-%.

4. The formable composition according to claims 2 or 3, wherein component (B) is present in a quantity of 50 to 65 wt-%.

5. The formable composition according to claims 1 to 4, characterised in that the heavy metal element is a rare earth metal or a metal of the sixth sub-group of the periodic system.

6. The formable composition according to claims 1 to 5, characterised in that the component (B) is yttrium fluoride, zirconium dioxide, lanthanum oxide, calcium tungstate or strontium tungstate, preferably calcium tungstate.

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7. The formable composition according to claims 1 to 6, characterised in that it is present in at least two part-compositions spatially separated from each other.

8. The formable composition according to claim 7, characterised in that at least one part-composition is present in solid, preferably powder form and at least one other part-composition in liquid or paste form.

9. The formable composition according to claim 8, characterised in that the solid part-composition contains the constituents (A) (a) and (B), and the liquid part-composition the constituents (A) (b), (A) (c) and optionally (A) (d).

10. The formable composition according to claim 8, characterised in that the solid part-composition contains the constituents (A) (a), (A) (b) and (B), and the liquid part-composition the constituents (A) (c) and optionally (A) (d).

11. The formable composition according to claim 8, characterised in that the solid part-composition contains the constituents (A) (a), (A) (b), optionally (A) (d) and (B), and the liquid part-composition the constituent (A) (c).

12. The formable composition according to claims 1 to 11, wherein the composition is used as filling material for dental root canals.

DATED this 5th day of October 1993

THERA PATENTS-VERWALTUNGS GmbH
Patent Attorneys for the Applicant:

F.B. RICE & CO.