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COMMONWEALTH of AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

AMENDED

^K
We DENTSPLY GmbH
of Eisenbahnstrasse 180,
D-6072 Dreieich,
Federal Republic of Germany.



hereby apply for the grant of a Standard Patent for an invention entitled:

"OPAQUE DENTAL CERAMIC MATERIAL"

LODGED AT SUB-OFFICE
26 APR 1988
Melbourne

which is described in the accompanying ~~provisional~~ complete specification.

Details of basic application(s):—

<u>Number</u>	<u>Convention Country</u>	<u>Date</u>
018,211	UNITED STATES OF AMERICA	24th February 1987
109,140	UNITED STATES OF AMERICA	15th October 1987

APPLICATION ACCEPTED AND AMENDMENTS

ALLOWED 18 - 10 - 90

The address for service is care of DAVIES & COLLISON, Patent Attorneys, of 1 Little Collins Street, Melbourne, in the State of Victoria, Commonwealth of Australia.

Dated this 26th day of April 19 88

To: THE COMMISSIONER OF PATENTS

H. M. Rimington
.....
(a member of the firm of DAVIES &
COLLISON for and on behalf of the Applicant).

Davies & Collison, Melbourne and Canberra.

COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952
DECLARATION IN SUPPORT OF CONVENTION OR
NON-CONVENTION APPLICATION FOR A PATENT

Insert title of invention.

In support of the Application made for a patent for an invention
entitled: "Opaque Dental Ceramic Material"

Insert full name(s) and address(es)
of declarant(s) being the appli-
cant(s) or person(s) authorized to
sign on behalf of an applicant
company.

I, Edward J. Hanson, Jr., of
~~We~~ Dentsply GMBH
Eisenbahnstrasse 180
PO Box 101074
D-6072 Dreieich
FEDERAL REPUBLIC OF GERMANY

Cross out whichever of paragraphs
1(a) or 1(b) does not apply
1(a) relates to application made
by individual(s)
1(b) relates to application made
by company; insert name of
applicant company.

do solemnly and sincerely declare as follows :-

1. (a) ~~I am~~ ~~the applicant~~..... ~~for the patent~~
~~We are~~
or (b) I am authorized by Dentsply GMBH

the applicant..... for the patent to make this declaration on ~~its~~ ~~their~~ behalf.

2. (a) ~~I am~~ ~~the inventor~~..... ~~of the invention~~
~~We are~~
or (b) Michael Herrn POLZ
Waldmullerstr. 12.
85020 Erlangen,
Federal Republic of Germany.

~~is~~ the actual inventor..... of the invention and the facts upon which the applicant.....
~~are~~
~~is~~ entitled to make the application are as follows :-
~~are~~

State manner in which applicant(s)
derive title from inventor(s)

The actual inventor has assigned the invention to
said applicant.

Cross out paragraphs 3 and 4
for non-convention applications.
For convention applications,
insert basic country(s) followed
by date(s) and basic applicant(s).

3. The basic application..... as defined by Section 141 of the Act ~~was~~ made
in United States of America on the February 24, 1987 ~~were~~
by ~~Dentsply GMBH~~ (U.S.S.N. 018,211) Michael Herrn Polz
in United States of America on the October 15, 1987
by Michael Herrn Polz (U.S.S.N. 109,140)
in on the
by

4. The basic application..... referred to in paragraph 3 of this Declaration ~~was~~
the first application..... made in a Convention country in respect of the invention the subject ~~were~~
of the application.

Insert place and date of signature.

Declared at York, PA 17405 this 23rd
U.S.A.

day of December, 1987

Signature of declarant(s) (no
attestation required)

Edward J. Hanson, Jr.
EDWARD J. HANSON, JR.
Patent Counsel

Note: Initial all alterations.

(12) PATENT ABRIDGMENT (11) Document No. AU-B-12043/88
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(54) Title
OPAQUE DENTAL CERAMIC MATERIAL

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(56) Prior Art Documents
EP 152337
EP 119062
US 4064311

(57) Claim

1. A method for coating a metal structure for a dental appliance comprising the steps of:

(a) coating said metal structure with an opaque ceramic paste, said opaque ceramic paste comprising

(1) a ceramic powder having a particle diameter of less than 50 μm in which 10% to 20% of said powder has a grain size less than 2 μm and

(2) an organic liquid having a boiling point below 300°C;

(b) dusting said opaque ceramic paste with a coarse ceramic powder having an average grain size of from 40 μm to 100 μm , said powder having thermal stability such that at least a substantial part of said grain structure is maintained under the conditions of firing said coating;

(c) applying at least one additional layer of ceramic opaque paste; and

(d) firing said at least one additional layer of ceramic opaque paste.

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2. The method according to claim 1 in which said organic liquid is selected from the group comprising glycerol, glycol, derivatives thereof or dimethylsulfoxide, and said ceramic paste contains a fine powder of SnO_2 , CeO_2 , TiO_2 , ZrO_2 , ZrSiO_4 or mixtures thereof.

7. A kit for preparing a dental appliance comprising;

(a) at least one pre-formed ready to use opaque ceramic paste, said opaque ceramic paste comprising

(1) a ceramic powder having a particle diameter of less than 50 μm in which 10% to 20% of said powder has a grain size less than 2 μm and

(2) an organic liquid having a boiling point below 300°C and

(b) a ceramic powder having an average grain size of from 40 μm to 100 μm , in which said ceramic powder has a thermal stability such that at least a portion of said grain structure is maintained under the conditions of firing.

PATENT ACT 1952COMPLETE SPECIFICATION(ORIGINAL)FOR OFFICE USE

This document contains the
amendments made under
Section 49 and is correct for
printing

CLASSINT. CLASS

Application Number:
Lodged:

Complete Specification Lodged:
Accepted:
Published:

Priority:

Related Art:

NAME OF APPLICANT: DENTSPLY GmbH

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NAME(S) OF INVENTOR(S) M.H. POLZ

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1 Little Collins Street, Melbourne, 3000.

COMPLETE SPECIFICATION FOR THE INVENTION ENTITLED:

"OPAQUE DENTAL CERAMIC MATERIAL"

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

OPAQUE DENTAL CERAMIC MATERIAL

BACKGROUND OF THE INVENTION

An opaque dental ceramic (porcelain) paste for applying to dental substructures, to be used in the preparation of ceramic dental appliances, such as crowns and bridges, and a method of using the same are provided.

When crowns, bridges and other metal dental substructures (copings) are to be veneered, the dental technician must first apply and fire a layer of opaque ceramic paste. This layer ensures a good bond to the veneering ceramic and, in addition, masks the unfavorable metal color of the substructure which is necessary to obtain a good aesthetic appearance.

Before the application of the opaque paste, an opaque slurry may optionally be fired on. For this purpose a thin suspension of ceramic opaque is mixed, applied and fired.

Conventional opaque ceramic paste consists of a pulverized opaque ceramic powder which is mixed with water, or a special modeling liquid, by the dental technician. The opaque powder itself consists of ground glass frits, which, owing to their chemical

compositions can be melted at temperatures below 1000°C and opacifying agents. During firing, leucite is partially crystallized out, thus the thermal expansion of the glass is adapted to the thermal expansion of the metal. A high portion of opacifiers ensures a good masking of the dark metal. The opaque materials are sold in several shades since they form the color basis for the desired tooth shade.

In preparing the opaque ceramic paste, the dental technician must adjust the consistency of the paste to obtain a paste which is sufficiently viscous so as to adhere to the metal substructure without sagging, but not so viscous that it cannot be easily applied. This procedure involves much trial and error and is very time consuming.

Conventional opaque application requires much time and skill because a very even layer thickness has to be achieved. If the layer of ceramic opaque is too thin, the metal substructure shines through, when the opaque is too thick, there is not enough space left for the full application of the subsequent body and enamel layers, which results in a diminished aesthetic affect.

Accordingly, there is a need in the art for an opaque paste, and a method, which makes it possible to avoid the time consuming procedure of mixing the paste in the laboratory, and makes it possible to apply

opaque ceramic paste more easily and more consistently, using fewer steps, to dental substructures and whereby an even layer thickness is achieved.

SUMMARY OF THE INVENTION

The present invention provides a method for coating a metal substructure for a dental appliance which comprises applying an opaque ceramic paste to the metal substructure, dusting the applied opaque paste with a coarse ceramic powder having an average grain size of from about 40 um to 100 um, firing the opaque, and applying additional ceramic and firing as needed. The ceramic powder used for the dusting must have a thermal stability such that grain structure is maintained under the conditions of firing. The method may comprise the additional step of using a preformed paste made by mixing a ceramic powder with an organic liquid such as glycerol. At least one additional layer of ceramic paste may then be added to the fired opaque, and said additional layer may optionally be applied using a paste made by mixing a ceramic powder with an organic liquid. Preferably the ceramic paste will be pre-formed and will be loaded into a package in which it can be stored, and from which it can be easily dispensed.

A kit is also provided which contains the preformed, ready to use opaque paste, the coarse ceramic powder, and optionally other ceramic materials that are needed to complete the building of a dental appliance.

Using the method, preformed paste, and the kit of the invention, it is possible for the dental technician to build a dental appliance such as a crown or a bridge using fewer steps, less time and less tedious methods. The preformed paste provided eliminates the need for time consuming trial and error mixing of a paste in the laboratory. The assured quality control of the paste that is used, and the method in which it is used lessens the possibility of applying an opaque layer that is too thin or too thick.

THE PRIOR ART

U. S. Patent 4,064,311, to McLean et al, teaches a process for a ceramic article which comprises firing porcelain onto a metal substrate. The metal substrate has an adherent layer of metal oxide deposited thereon which is wetted by the porcelain in the fused state.

U. S. Patent 4,557,691, to Martin et al, teaches an opaque porcelain paste comprising an opaque porcelain powder mixed with an aqueous colloidal

dispersion of urethane polymer. The paste can be applied as the first layer to a dental coping, and does not need to be fired prior to the addition of the body porcelain layers.

European Patent Application 0,119,062 teaches a storable paste-like material for use in preparing porcelain dental prostheses comprising a porcelain powder, water, and a small amount of finely divided ceramic material that overcomes the natural separation of the mixture of porcelain powder and water.

DETAILED DESCRIPTION OF THE INVENTION

The ceramic powders used in the present invention broadly constitute a known class of compositions. Conventionally, the powders used in making dental ceramic pastes have a grain size below about 60 um. In the ceramic powder used in the paste of the present invention, grain size is kept below about 50 um and preferably below about 40 um and in addition, powders of a grain size less than about 2 um are mixed therewith. Powders having an average grain size in the range of about 40 to 100 um are used in a dusting step.

In the method of the invention, either the powder used to make the opaque ceramic paste is ground

to a finer grain size than usual, or a portion of very fine powder having a grain size below about 2 μm is added to the opaque ceramic powder, such that between about 10% and 20% of the ceramic powder comprises a ceramic powder having a grain size below about 2 μm . In the case where very fine powder is added to the opaque ceramic powder, the fine powder added can be a very fine opaque frit or an opacifier such as CeO_2 , ZrSiO_4 , SnO_2 , ZrO_2 , or TiO_2 or mixtures thereof. As these opacifiers are supplied by the manufacturers in very small grain size, they need not be ground again.

In the method of the invention, the opaque powder is mixed with an organic liquid having a boiling point below 300°C to form a paste. The organic liquid used should not extend the firing times required and should not generate any hazardous gases during firing. Organic liquids that may be used in the method of the invention may be selected from the glycerols, glycols, derivatives thereof, or dimethylsulfoxide.

Particularly preferred is glycerol. Additives that increase the viscosity of the paste, such as alginates and stabilizing salts can be used. The consistency of the paste must be adjusted so that it can be applied to a metal substructure in an even layer with one stroke of the brush.

Using the paste of the invention as described eliminates the need for multiple application of the opaque slurry and firing steps as described in the prior art.

For convenience, it is preferred that the opaque ceramic paste be preformed and packaged in tubes or syringes so that required quantities can be easily extruded by the technician. Pre-forming the paste at the factory ensures that a paste having a specific viscosity and composition for the purpose it is to be used is consistently produced, thus avoiding the time consuming preparation of the paste in the laboratory. The addition of or presence of the fine grain particles, i.e. below 2 μm in diameter, helps prevent separation of the organic liquid from the dental powder in the paste while it is being stored and improves the spreadability of the paste.

After a layer of paste has been applied, the coated substructure is dusted with a layer of coarse ceramic powder, having an average grain size of between about 40 μm and 100 μm . In the dusting step, the coarse ceramic powder is taken up with a wide, dry brush. The brush is tapped above the object and the coarse grains of powder are thus released onto the freshly applied paste. Other means of providing a dusting will be apparent to those skilled in the art.

The coarse ceramic powder used preferably is chosen such that it has thermal stability under the conditions required for firing the ceramic paste composition. That is, the coarse grains will have properties such that they will form a strong sintered bond with the ceramic paste when the substructure is fired, but the grains will not be significantly melted or distorted by the firing so that a coarse grainy surface similar to that of sandpaper will be obtained.

Alternatively, when extra large grains of powder are used in the dusting step, ceramic powders may be chosen having a thermal stability such that a substantial portion of the grain structure is retained during firing, so that the sandpaper consistency of the surface, described above, is obtained.

A second layer of ceramic paste may then be applied to the substructure, filling the gaps between the protrusions of the coarse grains on the surface of the ceramic opaque, and fired.

Also, the second layer of ceramic, prior to firing, may be stained, to imitate anomalies in teeth. As is known to those skilled in the art, natural teeth are not perfectly smooth and do not have perfect consistency of color. Accordingly, when artificial teeth are made having perfect consistency, they do not look natural. To avoid this problem, and to provide a

natural appearance, artificial teeth, after they are fired, are often coated with a stain paste comprising a fine ground glass flux and pigments and fired again. During firing the stain paste fuses to the ceramic to provide a stained surface fused to the ceramic. In prior art methods of applying opaque, a first firing is required before the application of stain paste, apparently because the unfired ceramic is not stable enough to accommodate the "wet" stain paste. Using the ceramic paste and method of the invention, the stain paste may be applied to the second layer of ceramic before firing, reducing further the number of steps required to produce a finished product. As is known to those skilled in the art, the stain paste can be prepared by mixing a dry preparation of stain powder (fine ground glass flux and pigments) with a modeling liquid. According to the present invention, the modeling liquid may be an organic liquid having a boiling point less than 300°C such as glycerol, glycol, derivatives thereof, or dimethylsulfoxide. According to the present invention, the stains can be blended with the unfired layer of ceramic before firing, if necessary.

Alternatively or additionally, the pigments may be printed onto a substrate, parchment or flammable polymer for example, and placed on the ceramic before

firing. During firing the substrate burns off or evaporates leaving the pigments fused to the ceramic.

Accordingly, stains can be applied to the dental appliance without the need for an additional firing.

As is known to those skilled in the art, the first paste layer used may be made especially opaque, in order to completely mask the metal which it covers, and formulated to form a good bond with the metal. The second layer may be shaded according to the desired tooth shade. Dentin and enamel layers may be added in due course.

The coarse ceramic grains distributed on the first layer of ceramic opaque simplifies the addition of the second layer of ceramic paste since the technician need only concentrate on filling the gaps between the grains to achieve an even layer. Further, like bricks in a wall that overlap end to end, the grains serve as posts or anchors to improve the bonding of the next layer of ceramic.

In the second layer of opaque paste, which is applied to the spaces between the coarse grains, the use of additional opacifying oxides such as TiO_2 or SnO_2 in the composition is not desirable because of their high opacifying effect. To prevent separation of the dental powder from the modeling liquid in the paste

used in the second layer, it is preferred that about 3% of a hydrophobic aerosil (such as Degussa R 972) be added to the organic liquid (preferably glycerol). The spreadability of this paste is not as good as that of the first layer because of the absence of the fine (less than 2 um) particles, but high spreadability of the second layer is not needed because application of the second layer is made easy because of the presence of the coarse grains fired on to the first layer of paste.

The rough surface, resulting from the use of the coarse ceramic particles, can also be used in the case where a silane bonding agent is used for applying and polymerizing an acrylic resin veneer. The present method can also be used in the adhesive bonding technique. Both methods are well known in the art.

The method of the present invention has the advantages that it saves the dental technician considerable time, because application of the different layers of paste is made easier. There is less waste of material because the technique is simplified and the time spent on trial and error mixing of the paste in the laboratory is substantially eliminated. The opaque layers may be made especially thin and even, thus leaving enough room for body and enamel layers so that a good aesthetic result can be obtained. Also, since

the technique is made simple, and more even layers are obtained, the possibility of faults developing is reduced.

As an example of the composition that may be used for the first opaque layer, the following is provided:

EXAMPLE

Composition of the opaque for the first layer:

SiO ₂	42 weight-%
Al ₂ O ₃	12 "
K ₂ O	8 "
Na ₂ O	4 "
Li ₂ O	0.5 "
CaO	1.5 "
B ₂ O ₃	1 "
ZrO ₂	1 "
SnO ₂	10 "
TiO ₂	20 "

All oxides are ingredients of a ground glass frit. Only the TiO₂ is admixed to insure the presence of a fine powder, which is needed to insure the good spreadability of the paste.

The composition of the opaque paste for the second layer will differ slightly from the above formula because part of the opacifiers will be replaced by pigments in order to produce the desired tooth shade.

The opaque, not including the TiO_2 , has the following grain size distribution:

< 5	< 12	< 24	< 40	um
21	66	98	100	%

On the average, TiO_2 has a grain size less than about 1 um.

The paste has the following composition:

opaque powder	67.7	weight-%
glycerol	32.0	"
alum or other stabilizing salt	0.3	"

The coarse ceramic powder distributed on the opaque paste after it is applied to the dental appliance substructure has the following composition:

SiO_2	56	weight-%
Al_2O_3	13	"
K_2O	9	"
Na_2O	4	"
CeO_2	18	"

The sieve fraction used: < 80 um > 40 um

The paste and dusting powder described in the Example will be fired at about 980°C.

For convenience, the materials used in the method of the invention may be provided in kit form.

The preformed opaque paste, with known firing properties, may be packaged in a kit with a coarse ceramic powder that has the thermal stability required

by the present method under the firing conditions required to fire the pre-formed paste. If more than one ceramic paste having different properties for different applications, and having different firing requirements, and more than one coarse ceramic powder are provided in the same kit, the packages containing them can be color coded so that the correct coarse ceramic powder is used with the correct ceramic paste. As will be apparent to those skilled in the art, many specific ceramic compositions may be matched with many specific dusting powders by comparing physical properties that are known in the art.

In addition to the opaque paste, the kit may be provided with additional ceramics for use in the body layers and the dentin and enamel layers and other conventional materials as required. To the degree possible, these materials may be provided in a preformed paste, or in conventional states. For example, as described above, a paste composition of the second opaque layer may be provided.

While specific embodiments of the invention have been described herein, it will be apparent to those skilled in the art that the present invention may be modified and variously practiced without going outside the scope of the following claims.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A method for coating a metal structure for a dental appliance comprising the steps of:

(a) coating said metal structure with an opaque ceramic paste, said opaque ceramic paste comprising

(1) a ceramic powder having a particle diameter of less than 50 μm in which 10% to 20% of said powder has a grain size less than 2 μm and

(2) an organic liquid having a boiling point below 300°C;

(b) dusting said opaque ceramic paste with a coarse ceramic powder having an average grain size of from 40 μm to 100 μm , said powder having thermal stability such that at least a substantial part of said grain structure is maintained under the conditions of firing said coating;

(c) applying at least one additional layer of ceramic opaque paste; and

(d) firing said at least one additional layer of ceramic opaque paste.

2. The method according to claim 1 in which said organic liquid is selected from the group comprising glycerol, glycol, derivatives thereof or dimethylsulfoxide, and said ceramic paste contains a fine powder of SnO_2 , CeO_2 , TiO_2 , ZrO_2 , ZrSiO_4 or mixtures thereof.

3. The method according to claim 1 or claim 2 which comprises the further step of preparing the ceramic opaque paste used for at least one of said additional layers of ceramic by mixing a dental ceramic powder with an organic liquid.

4. The method according to any preceding claim which comprises the step of applying a second layer of opaque



paste in such a manner that the gaps between projecting grains of coarse ceramic material are filled.

5. The method according to claim 4 which comprises the step of applying a stain paste to said second layer of opaque paste.

6. The method according to claim 5 which comprises the step of preparing a stain paste by mixing a dry preparation of stain powder with an organic liquid selected from the group comprising glycerol, glycol, derivatives thereof or dimethylsulfoxide.

7. A kit for preparing a dental appliance comprising;

- (a) at least one pre-formed ready to use opaque ceramic paste, said opaque ceramic paste comprising
 - (1) a ceramic powder having a particle diameter of less than 50 μm in which 10% to 20% of said powder has a grain size less than 2 μm and
 - (2) an organic liquid having a boiling point below 300°C and
 - (b) a ceramic powder having an average grain size of from 40 μm to 100 μm , in which said ceramic powder has a thermal stability such that at least a portion of said grain structure is maintained under the conditions of firing.

8. The kit according to claim 7 in which said pre-formed opaque paste is packaged in a syringe for easy dispensing of said paste and said kit further includes materials for conventional dentin and enamel layers.

9. The kit according to claim 7 in which said organic liquid is selected from the group comprising glycerol, glycol, derivatives thereof or dimethylsulfoxide.



10. The kit according to claim 7 in which said preformed opaque ceramic paste is made using a ceramic powder having a particle diameter of less than about 40 μm , said powder comprising SnO_2 , CeO_2 , TiO_2 , ZrO_2 , ZrSiO_4 or mixtures thereof.

11. The kit according to claim 7 wherein said pre-formed opaque ceramic paste comprises:

(a) a dental ceramic powder wherein

(1) 80% to 90% of said powder comprises oxides of a ground glass frit having a particle size less than 40 μm and

(2) between 10% to 20% of ground glass frit or an opacifier having a particle size less than 2 μm and

(b) glycerol.

12. A method for coating a metal structure for a dental appliance, a kit for preparing the appliance and a preformed opaque ceramic paste substantially as hereinbefore described with reference to the examples.

DATED this 1st day of October 1990.

DENTSPLY GMBH

By Its Patent Attorneys

DAVIES & COLLISON

