PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau.

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :		(11) International Publication Number:
A61K 6/10, A61C 9/00	A1	WO 93/17654
		(43) International Publication Date: 16 September 1993 (16.09.93)

(21) International Application Number: PCT/US93/01930

(22) International Filing Date: 2 March 1993 (02.03.93)

(30) Priority data:
844,787 2 March 1992 (02.03.92) US

(71)(72) Applicant and Inventor: PARADISO, Vincent [US/US]; 98 Chapin Road, New Milford, CT 06776 (US).

(74) Agent: BOWERSOX, Leonard, D.; Watson, Cole, Grindle & Watson, 1400 K Street, N.W., Suite 725, Washington, DC 20005 (US).

(81) Designated States: JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
With amended claims.

(54) Title: DENTAL IMPRESSION MATERIALS CONTAINING QUADRI-FUNCTIONAL SILOXANE POLYMERS

(57) Abstract

Dental impression materials have improved tear strength and resist tearing upon removal from a set of teeth, especially form a dramatically undercut set of teeth. The dental impression materials incorporate a mono- and quadri-functional (MQ) siloxane component into a silicone-based dental impression material composition. A method of taking a dental impression uses the modified materials.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo			SE	Sweden
CH	Switzerland	KR	Republic of Korea	SK	Slovak Republic
CI	Côte d'Ivoire	KZ	Kazakhstan	SN	Senegal
CM	Cameroon	LI	Liechtenstein	SU	Soviet Union
CS	Czechoslovakia	LK	Sri Lanka	TD	Chad
CZ	Czech Republic	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	UA	Ukraine
DK	Denmark	MG	Madagascar	US	United States of America
ES	Spain	ML	Mali	VN	Viet Nam
FI	Finland	MN	Mongolia		

DENTAL IMPRESSION MATERIALS CONTAINING QUADRI-FUNCTIONAL SILOXANE POLYMERS

BACKGROUND OF THE INVENTION

The present invention is based upon the discovery that dental impression materials can be produced which have increased tear strength by adding a mono- and quadri-functional siloxane polymer to the material prior to taking a dental impression.

The use of siloxane polymers in dental impression materials has been taught in the prior art. U.S. Patent Nos. 4,657,959 and 4,752,633 disclose dental impression materials which contain silicone polymers having mono- and di-functional silicon atoms. U.S. Patent No. 4,877,854 discloses many polyorganosiloxane polymers useful as dental impression materials. These dental impression materials have suffered from a low tear strength causing problems when removing the molding materials from a set of teeth, particularly teeth having severe undercuts.

The silicone polymers which have been used are based upon linear siloxane chains having functional end groups which enable cross-linking at the chain ends. Little or no cross-linking takes place along the length of the chains.

In order to improved the tear strength of these prior impression materials, various fillers have been added, particularly hydrophobic fillers.

U.S. Patent No. 4,359,565 discloses the use of a diatomaceous earth filler in combination with a polydimethyl siloxane silicone polymer. The polydimethyl siloxanes disclosed container either vinyl end groups or dimethylhydridosilyl end groups. It is known that when impressions are made with siloxane materials, the final product has to date exhibited poor tear strength.

Vinylsiloxane systems have been used for impression materials since they are odorless, tasteless

and dimensionally stable. Unfortunately, currently available vinylsiloxane impression materials also exhibit poor tear strength.

A need exists for a vinylsiloxane dental impression material having improved tear strength and a resistance to tearing upon removal from a set of teeth.

SUMMARY OF THE INVENTION:

The present invention overcomes the problems encountered by the prior art dental impression materials by providing a dental impression material having improved tear strength and a resistance to tearing upon removal from a set of teeth, especially from a dramatically undercut set of teeth. The present invention provides a dental impression material having improved tear strength and resistance by incorporating a mono- and quadri-functional (MQ) siloxane component into a silicone-based dental impression material composition. The dental impression materials of the present invention comprise:

(A) about 25% to about 90% by weight vinyl end-stopped linear siloxane polymer having a viscosity of from about 100 to about 1,500,000 cps at 25°C, or blends of such polymers;

(B) a siloxane resin containing mono- and quadri-functional silicon atoms, referred to as an MQ resin, present in an amount of up to about 75 percent by weight such that the total of Components (A) and (B) is from about 15% to about 90% of the total weight of the dental impression material;

(C) up to about 85% by weight at least one filler selected from the group consisting of silica, cornstarch, quartz, quartz flours, calcium silicate, calcium carbonate, calcium sulfate, pumice flours,

crystoballite flours, hydrated alumina, diatomaceous earth, talc and precipitated and pyrogenically produced silicon dioxide;

(D) from about 1 percent to about 10 percent by weight methyl hydrogen polysiloxane cross-linking agent having a viscosity of less than about 500 cps at 25°C;

(E) platinum containing catalyst present in an amount of up to about 6% by weight; and

(F) up to about 4% by weight coloring agent.

By incorporating an MQ component in accordance with the present invention, a dental impression material is provided which can cure quickly in a patient's mouth and form a strong and lasting impression of an intraoral structure which remains intact after removal.

DETAILED DESCRIPTION OF THE INVENTION:

The tear strength of a silicone composition can be increased by adding an MQ component to the composition. It is believed that the quadri-functionality of the MQ resins enables a great deal of cross-linking within a silicone composition. In strictly linear silicone polymers which react only at their end groups, very little cross-linking along the chain takes place. With an MQ polymer, however, a matrix of cross-links is provided which adds to the strength and durability of an entire composition.

The present invention relates to incorporating an MQ-containing siloxane component into a silicone polymer system, and using the system to take a dental impression of an intraoral structure. An intraoral structure is defined herein as a set of teeth, a single tooth, a set of dentures, a set of gums, a prosthetic device, or the like. The materials of the present invention may also be used as bite registration

materials. A bite registration is also herein considered to be included as an impression of an intraoral structure.

According to a preferred embodiment of the present invention, the dental impression material comprises a siloxane composition having:

(A) about 25% to about 90% by weight vinyl end-stopped linear siloxane polymer having a viscosity of from about 100 to about 1,500,000 cps at 25°C, or blends of such polymers;

(B) a siloxane resin containing mono- and quadri-functional silicon atoms, present in an amount of up to about 75 percent by weight such that the total of Components (A) and (B) is from about 15% to about 90% of the total weight of the siloxane composition;

(C) up to about 85% by weight at least one filler selected from the group consisting of silica, cornstarch, quartz, diatomaceous earth, talc and silica gel;

(D) from about 1 percent to about 10 percent by weight methyl hydrogen polysiloxane cross-linking agent having a viscosity of less than about 500 cps at 25°C;

(E) platinum containing catalyst present in an amount of up to about 6% by weight; and

(F) up to about 4% by weight coloring agent.

Component (A) can generally be described as a siloxane polymer having functional end-stops. In a preferred embodiment, component (A) comprises a vinyl-dimethyl terminated polydimethylsiloxane. Other polyorganosiloxanes may also be used.

Depending upon what type of dental impression material is desired, the chain length of Component (A) may vary such that a wide variety of viscosities may be employed. For a mono-phasic material from which a final dental impression is taken in a single step, a

low to medium viscosity impression material is desired. A medium viscosity or "medium body" impression material typically includes a polyorganosiloxane polymer for Component (A) which has a viscosity of from about 100 to about 100,000 cps at 25°C. Typical polymers which are readily available on the market include those having viscosities of 100, 200, 1,000, 2,000, 10,000, 60,000, 65,000 and 165,000 cps at 25°C. Any of these may be used for Component (A) of a medium body dental impression material.

Many of the medium body materials may be prepared and applied from a tray or from a syringe. To facilitate application of the heavier viscosity materials, such as those containing a 1,000 to 165,000 cps siloxane polymer for Component (A), preparation and application from a tray is preferred.

Thicker viscosity materials are called "tray weight" or "heavy body" materials and typically contain a polyorganosiloxane for Component (A) which has a viscosity of from about 1,000 to about 165,000 cps at 25°C. A viscosity of from about 10,000 to about 100,000 is preferred for component (A) in a heavy body material. Tray weight or heavy body materials are generally not preferred for taking a one-step impression since they provide much less detail than is usually desired.

Tray weight or heavy body materials are commonly used for two-step impression methods. According to a two-step method, a heavy body is used to take a preliminary impression of a tooth, set of teeth, or any portion of dentition. The impression material around the preparation is then relieved (slightly enlarged), e.g. by carving, and filled with a much lighter weight material as described below. The two-layer impression material is then reapplied to the dentition so as to

form a two-layer impression having even greater detail around the preparation.

Putties may also be used for two-step impressions and are preferred in some cases. A putty-weight material may comprise a polyorganosiloxane for Component (A) having a viscosity of from about 100 to about 1,500,000 cps at 25°C. The heavier viscosity polymers are preferably used for Component (A) when formulating a putty-weight material. A putty-weight impression material generally has a much higher filler content than any of the lighter weight materials.

Lighter viscosity compositions are used during the second step of a two-step impression process. These compositions provide the highest detail of the dental impression materials due to their fluidity. These lightweight materials are generally called "syringe weight" and contain very little filler. Syringe weight materials typically contain a polyorganosiloxane for Component (A) which has a viscosity of about 100 to about 65,000 cps at 25°C. Syringe weight materials containing Component (A) having a viscosity of up to 65,000 cps at 25°C may be used but are not preferred. According to some preferred embodiments, the syringe weight material comprises Component (A) having a viscosity of 100 to 10,000 cps at 25°C.

The viscosity of any of the different weight compositions can be controlled by varying the viscosity of the silicone oil, the ratio of silicone oil to filler, the affinity of the filler for the silicone oil (oil absorption number) and the density and specific surface area of the filler.

As can be seen, the amounts and viscosities of Component (A) may vary depending upon the desired application of the dental impression material. In general, the lower viscosity of the polymer used, the

higher the durometer of the cured material. Dental materials containing two or more polymers having different viscosities from each other may also be employed for Component (A).

The improved tear strength and tear resistance of the dental impression materials of the present invention can be attributed to the incorporation of Component (B), a siloxane resin containing mono- and quadri-functional silicon atoms. These silicon atoms are considered mono- and quadri-functional based on the degree of functionality of methylsilicon or other organic substituent subunits. When clusters of quadri-functional silicon atoms are very small, almost all of the silicons are on the outer surface and thus have unattached SiOH groups sticking out. When these SiOH groups are capped off with Me_3Si - or M units, an MQ resin results.

At the lower molecular weight end of MQ resins are tetrakis(trimethylsiloxy)silane, $(Me_3SiO)_4Q$, and tris(trimethylsiloxy)silanol, $(Me_3SiO)_3SiOH$ or M_3Q^{OH}. At the upper end of the weight range are gels. The most useful materials are those with a molecular weight range of from about 1,000 to about 10,000. A broader range of materials may also be used, for instance, materials in the molecular weight range of about 100 to about 100,00. The range of MW in the product, or polydispersity, is usually broad and somewhat dependent upon the method of preparation.

Based upon the total weight of the impression material, Component (B) may be present in an amount of up to about 75 parts by weight. Preferably, Component (B) is present in an amount of from about 1 to about 25 percent by weight, more preferably from about 5 to about 15 percent by weight. In a particularly preferred embodiment, Component (B) is present from

about 5 to about 7 percent by weight. Component (B) preferably has a viscosity of from about 4,000 to about 6,000 cps at 25°C.

The combination of Components (A) and (B) should make up from about 15 to about 90 percent by weight of the total impression material formulation.

Component (C) is a filler which may be added to the dental impression material in an appropriate amount depending upon the viscosity desired. As discussed above with respect to Component (A), very little filler is added to provide a syringe weight material whereas a large amount of filler is added to provide a putty-weight material. Generally, the filler is added in amounts of up to about 85 percent by weight based upon the total weight of the material. For a syringe weight material, between about 5 and about 35 percent by weight Component (C) are added. For a putty-weight material, about 55 to about 85 percent by weight Component (C) is added. The amount of filler and the viscosity of Component (A) may be varied within their appropriate ranges to provide the various weight dental impression materials discussed herein.

The filler is generally selected from silica, silica gel, cornstarch, quartz, quartz flours, calcium silicate, calcium carbonate, calcium sulfate, pumice flours, crystoballite flours, hydrated alumina, diatomaceous earth, talc and precipitated and pyrogenically produced silicon dioxide and other fillers known to those of ordinary skill in the art. High surface area fillers, e.g. 100 m^2/gm and higher, are preferred. One specific filler which may be used is in many of the compositions is Aerosil™ available from Degussa Company, Richfield Park, New Jersey.

Component (D) comprises a cross-linker containing hydride substituents off of a polysiloxane chain.

Preferred cross-linkers include methyl hydrogen polysiloxanes, preferably linear methyl hydrogen polysiloxanes. The cross-linking agent preferably has a viscosity of less than about 250 cps at 25°C and more preferably from about 25 to about 75 cps at 25°C. Preferably, up to about 50 percent of the substituents off of the siloxane chain are hydride substituents.

Component (D) is preferably present in an amount of between 1 and about 10 percent by weight depending upon the viscosity and the desired degree of cross-linking. Greater amounts of cross-linker are employed with formulations for harder impression materials, e.g. bite registration materials. More preferably, from about 3 to about 8 percent by weight Component (D) is employed. In one embodiment, when about 3 to about 8 percent by weight Component (D) is employed, the cross-linker has a viscosity of about 40 centipoise at 25°C.

Component (E) is a platinum catalyst used to catalyze the cross-linking of the siloxane components within the dental material. In a preferred embodiment, Component (E) is a vinyl-dimethyl terminated polydimethylsiloxane platinum complex. When mixed with the cross-linking agent and reactive polymers and fillers, the platinum catalyst allows the composition to cure relatively quickly such that the dental impression material does not need to remain within a patient's mouth for any extended period of time.

Since the platinum catalyst in the presence of cross-linker and reactive polymer and/or filler allows the composition to cure so quickly, it is separated from the cross-linking agent such that the dental impression material comprises two individual phases which are mixed just prior to use. The one phase contains the platinum catalyst while the other phase contains the cross-linking agent. Preferably,

Components (A) and (C) are divided among the two phases such that the viscosities of the two phases are substantially similar. Component (B) is added to a first phase which contains the cross-linker whereas the platinum catalyst is incorporated into the second phase.

Component (E) is preferably present in an amount of up to about 6 percent by weight depending upon the available vinyl reactive units in components (A) and (B). The more vinyl present in the uncured material, the more catalyst and cross-linker necessary. In a preferred embodiment, the platinum catalyst is added such that approximately 20 ppm of platinum is available in the material. The platinum catalyst is preferably a platinum complex containing vinyl-dimethyl terminated polydimethylsiloxane and platinum supplied from a platinum tetrachloride salt.

Component (F) is a coloring agent which facilitates inspection of the detail provided by the impression material. The coloring agent is preferably present in an amount of up to about 4 percent by weight, about 0.2 to about 4 percent being a more preferred range. Typical coloring agents used for Component (F) include FDC colors and iron oxides.

In order to substantially equalize the viscosities between the two phases, usually more filler is added to the phase containing the cross-linking agent than to the phase containing the platinum catalyst. This is especially useful when the cross-linking agent has a low viscosity e.g., about 40 centipoise at 25°C. The increased amount of filler in the phase containing the low viscosity cross-linking agent tends to increase the viscosity of the phase. It is preferred to have substantially equal viscosities between the two phases in order to facilitate miscibility when mixed just

prior to being applied on a patient's teeth. Most preferably, the two phases have identical viscosities.

Preferably, the two phases of a syringe weight material each have a viscosity in the range of from about 1 to about 125,000 cps at 25°C. For medium and heavy weight materials, the viscosities for each phase are preferably from about 75,000 to about 250,000 and about 200,000 to about 800,000 cps at 25°C, respectively. Putty weight materials preferably have viscosities in the range of from about 750,000 to about 1,500,000 cps at 25°C. Of course, it is preferred that the two phases of any weight material have similar, if not almost identical, viscosities.

Although the present invention has been described in connection with preferred embodiments, it will be appreciated by those skilled in the art that additions, modifications, substitutions and deletions not specifically described may be made without departing from the spirit and scope of the invention defined in the appended claims.

WHAT IS CLAIMED IS:

1. A dental impression material comprising a first siloxane composition molded into an impression of an intraoral structure, said first siloxane composition comprising:

(A) about 25% to about 90% by weight vinyl end-stopped linear siloxane polymer having a viscosity of from about 100 to about 1,500,000 cps at 25°C, or blends of such polymers;

(B) a siloxane resin containing mono- and quadri-functional silicon atoms and having a molecular weight of from about 100 to about 100,000, said resin present in an amount of up to about 75 percent by weight such that the total of Components (A) and (B) is from about 15% to about 90% of the total weight of the dental impression material;

(C) up to about 85% by weight at least one filler selected from the group consisting of silica, cornstarch, quartz, quartz flours, calcium silicate, calcium carbonate, calcium sulfate, pumice flours, crystoballite flours, hydrated alumina, diatomaceous earth, talc and precipitated and pyrogenically produced silicon dioxide;

(D) from about 1 percent to about 10 percent by weight methyl hydrogen polysiloxane cross-linking agent having a viscosity of less than about 500 cps at 25°C;

(E) platinum containing catalyst present in an amount of up to about 6% by weight; and

(F) up to about 4% by weight coloring agent.

2. A dental impression material as defined in claim 1, wherein Component (B) is present in an amount of between about 1 and about 25 percent by weight.

3. A dental impression material as defined in claim 1, wherein Component (B) is present in an amount of between about 5 and about 15 percent by weight.

4. A dental impression material as defined in claim 1, wherein Component (B) is present in an amount of between about 5 and about 7 percent by weight.

5. A dental impression material as defined in claim 1, wherein Component (A) has a viscosity of between about 100 and about 1,000 cps at 25°C.

6. A dental impression material as defined in claim 1, wherein Component (A) has a viscosity of between about 1,000 and about 10,000 cps at 25°C.

7. A dental impression material as defined in claim 1, wherein Component (A) has a viscosity of between about 10,000 and about 100,000 cps at 25°C.

8. A dental impression material as defined in claim 1, wherein Component (A) has a viscosity of between about 100,000 and about 1,500,000 cps at 25°C.

9. A dental impression material as defined in claim 1, wherein Component (A) is a vinyl-dimethyl terminated polydimethylsiloxane.

10. A dental impression material as defined in claim 1, wherein Component (E) is a vinyl-dimethyl terminated polydimethylsiloxane platinum complex.

11. A dental impression material as defined in claim 1, wherein Component (F) is at least one FDC color.

12. A dental impression material as defined in claim 1, wherein Component (F) is at least one iron oxide material.

13. A dental impression material as defined in claim 1, further comprising a second siloxane composition having:

(A) about 25% to about 90% by weight vinyl end-stopped linear siloxane polymer having a viscosity of from about 100 to about 1,500,000 cps at 25°C, or blends of such polymers;

(B) a siloxane resin containing mono- and quadri-functional silicon atoms and having a molecular weight of from about 100 to about 100,000, said resin present in an amount of up to about 75 percent by weight such that the total of Components (A) and (B) is from about 15% to about 90% of the total weight of the dental impression material;

(C) up to about 85% by weight at least one filler selected from the group consisting of silica, cornstarch, quartz, quartz flours, calcium silicate, calcium carbonate, calcium sulfate, pumice flours, crystoballite flours, hydrated alumina, diatomaceous earth, talc and precipitated and pyrogenically produced silicon dioxide;

(D) from about 1 percent to about 10 percent by weight methyl hydrogen polysiloxane cross-linking agent having a viscosity of less than about 500 cps at 25°C;

(E) platinum containing catalyst present in an amount of up to about 6% by weight; and

(F) up to about 4% by weight coloring agent,

wherein said second siloxane composition is a coating on top of said first siloxane composition and wherein said second siloxane composition has a

viscosity which is less than a viscosity of the first siloxane composition.

14. A method of taking a dental impression comprising:

applying a first dental impression material to an intraoral structure;

allowing said first dental impression material to substantially cure so as to maintain the impression of said intraoral structure when removed therefrom; and

removing said first dental impression material from said intraoral structure to form a dental impression, wherein said first dental impression material comprises:

(A) about 25% to about 90% by weight vinyl end-stopped linear siloxane polymer having a viscosity of from about 100 to about 1,500,000 cps at 25°C, or blends of such polymers;

(B) a siloxane resin containing mono- and quadri-functional silicon atoms and having a molecular weight of from about 100 to about 100,000, said resin present in an amount of up to about 75 percent by weight such that the total of Components (A) and (B) is from about 15% to about 90% of the total weight of the dental impression material;

(C) up to about 85% by weight at least one filler selected from the group consisting of silica, cornstarch, quartz, quartz flours, calcium silicate, calcium carbonate, calcium sulfate, pumice flours, crystoballite flours, hydrated alumina, diatomaceous earth, talc and precipitated and pyrogenically produced silicon dioxide;

(D) from about 1 percent to about 10 percent by weight methyl hydrogen polysiloxane cross-linking agent having a viscosity of less than about 500 cps at 25°C;

(E) platinum containing catalyst present in an amount of up to about 6% by weight; and

(F) up to about 4% by weight coloring agent.

15. A method as defined in claim 14, wherein said first dental impression material comprises a two-part system, said two-part system comprising:

part (I) Component (B), Component (D), a portion of Component (A) and a portion of Component (C); and

part (II) comprises Component (E), and the remaining portions of Components (A) and (C), wherein said method includes the step of mixing parts (I) and (II) to form said first dental impression material prior to applying said first dental impression material to said intraoral structure.

16. A method as defined in claim 14, wherein said method further includes the step of applying a second dental impression material to said dental impression to from a two-layer dental impression material, said second dental impression material comprising:

(A) about 25% to about 90% by weight vinyl end-stopped linear siloxane polymer having a viscosity of from about 100 to about 1,500,000 cps at 25°C, or blends of such polymers;

(B) a siloxane resin containing mono- and quadri-functional silicon atoms and having a molecular weight of from about 100 to about 100,000, said resin present in an amount of up to about 75 percent by weight such that the total of Components (A) and (B) is from about 15% to about 90% of the total weight of the dental impression material;

(C) up to about 85% by weight at least one filler selected from the group consisting of silica, cornstarch, quartz, quartz flours, calcium silicate,

calcium carbonate, calcium sulfate, pumice flours, crystoballite flours, hydrated alumina, diatomaceous earth, talc and precipitated and pyrogenically produced silicon dioxide;

(D) from about 1 percent to about 10 percent by weight methyl hydrogen polysiloxane cross-linking agent having a viscosity of less than about 500 cps at 25°C;

(E) platinum containing catalyst present in an amount of up to about 6% by weight; and

(F) up to about 4% by weight coloring agent,

said second dental impression material having a viscosity which is less than a viscosity of said first dental impression material;

applying the two-layer dental impression material to said intraoral structure;

allowing said second dental impression material of said two-layer dental impression material to substantially cure so as to maintain the intraoral impression when removed from the oral cavity; and

removing said two-layer dental impression material from said intraoral structure to form a two-layer dental impression.

AMENDED CLAIMS

[received by the International Bureau on 20 July 1993 (20.07.93);
original claims 1,13 and 14 amended;
remaining claims unchanged (5 pages)]

1. A dental impression material comprising a first siloxane composition, said dental impression material being molded into an impression of an intraoral structure, said first siloxane composition comprising the reaction product of:

(A) about 25% to about 90% by weight vinyl end-stopped linear siloxane polymer having a viscosity of from about 100 to about 1,500,000 cps at 25°C, or blends of such polymers;

(B) up to about 75% by weight siloxane resin containing mono- and quadri-functional silicon atoms and having a molecular weight of from about 100 to about 100,000, said resin present in an amount effective to increase the tear strength of said dental impression material, wherein the total of Components (A) and (B) is from about 15% to about 90% of the total weight of the dental impression material, said siloxane resin increasing the tear strength of the impression material by providing a matrix of cross-links enabled by the quadri-functionality of the resin, wherein the matrix of cross-links adds to the strength and durability of the entire composition;

(C) up to about 85% by weight at least one filler selected from the group consisting of silica, cornstarch, quartz, quartz flours, calcium silicate, calcium carbonate, calcium sulfate, pumice flours, cristobalite flours, hydrated alumina, diatomaceous earth and talc;

(D) from about 1 percent to about 10 percent by weight methyl hydrogen polysiloxane cross-linking agent having a viscosity of less than about 500 cps at 25°C;

(E) a catalytic amount of platinum containing catalyst; and

(F) up to about 4% by weight coloring agent.

2. A dental impression material as defined in claim 1, wherein Component (B) is present in an amount of between about 1 and about 25 percent by weight.

12. A dental impression material as defined in claim 1, wherein Component (F) is at least one iron oxide material.

13. A dental impression material as defined in claim 1, further comprising a second siloxane composition comprising the reaction product of:

(A1) about 25% to about 90% by weight vinyl end-stopped linear siloxane polymer having a viscosity of from about 100 to about 1,500,000 cps at 25°C, or blends of such polymers;

(B1) up to about 75% by weight siloxane resin containing mono- and quadri-functional silicon atoms and having a molecular weight of from about 100 to about 100,000, said resin present in an amount effective to increase the tear strength of said dental impression material, wherein the total of Components (A1) and (B1) is from about 15% to about 90% of the total weight of the dental impression material, said siloxane resin increasing the tear strength of the impression material by providing a matrix of cross-links enabled by the quadri-functionality of the resin, wherein the matrix of cross-links adds to the strength and durability of the entire composition;

(C1) up to about 85% by weight at least one filler selected from the group consisting of silica, cornstarch, quartz, quartz flours, calcium silicate, calcium carbonate, calcium sulfate, pumice flours, cristobalite flours, hydrated alumina, diatomaceous earth and talc;

(D1) from about 1 percent to about 10 percent by weight methyl hydrogen polysiloxane cross-linking agent having a viscosity of less than about 500 cps at 25°C;

(E1) a catalytic amount of a platinum containing catalyst; and

(F1) up to about 4% by weight coloring agent, wherein said second siloxane composition is a coating on top of said first siloxane composition and wherein said second siloxane composition has a

viscosity which is less than the viscosity of the first siloxane composition.

14. A method of taking a dental impression comprising:

applying a first dental impression material to an intraoral structure;

allowing said first dental impression material to substantially cure so as to maintain the impression of said intraoral structure when removed therefrom; and

removing said first dental impression material from said intraoral structure to form a dental impression, wherein said first dental impression material comprises:

(A) about 25% to about 90% by weight vinyl end-stopped linear siloxane polymer having a viscosity of from about 100 to about 1,500,000 cps at 25°C, or blends of such polymers;

(B) a siloxane resin containing mono- and quadri-functional silicon atoms and having a molecular weight of from about 100 to about 100,000, said resin present in an amount of up to about 75 percent by weight such that the total of Components (A) and (B) is from about 15% to about 90% of the total weight of the dental impression material;

(C) up to about 85% by weight at least one filler selected from the group consisting of silica, cornstarch, quartz, quartz flours, calcium silicate, calcium carbonate, calcium sulfate, pumice flours, cristobalite flours, hydrated alumina, diatomaceous earth, talc and precipitated and pyrogenically produced silicon dioxide;

(D) from about 1 percent to about 10 percent by weight methyl hydrogen polysiloxane cross-linking agent having a viscosity of less than about 500 cps at 25°C;

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/01930

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :A61K 6/10; A61C 9/00
US CL :Please See Extra Sheet.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 523/109; 524/862, 861, 734, 745, 788, 791, 789, 786, 588, 47, 442, 425, 423, 444, 437, 448, 451

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 5,064,891 (FUJIKI ET AL) 12 NOVEMBER 1991. Column 2, line 46-column 3, line 6, Examples 1 and 7, column 3, lines 15-56	1,5,6,9 & 12
Y	US, A, 4,035,453 (HITTMAIR ET AL) 12 JULY 1977. Column 2, line 1-column 4, line 30.	1-13
Y	US, A, 4,609,687 (SCHWABE ET AL) 02 SEPTEMBER 1986. Column 1, line 53-column 2, line 3.	14-16
A	US, A, 4,222,983 (AUGUST ET AL) 16 SEPTEMBER 1980.	1-16
A	US, A, 3,950,300 (HITTMAIR ET AL) 13 APRIL 1976	1-16

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be part of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
21 APRIL 1993	25 MAY 1993
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. NOT APPLICABLE	Authorized officer KAREN A. DEAN Telephone No. (703) 308-2351

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/01930

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

523/109; 524/862, 861, 734, 745, 788, 791, 789, 786, 588, 47, 442, 425, 423, 444, 437, 448, 451