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(54) Title: ELASTOMERIC STATE GLASS IONOMER CEMENT

(57) Abstract

The present invention provides an elastomeric material obtainable by curing a composition comprising a mixture of a liquid precursor of a glass ionomer cement and a powdered precursor of a glass ionomer cement, said liquid precursor comprising at least one polymerisable monomer present in a range of between 2 to 50 % by weight of said liquid precursor of a glass ionomer cement, a carboxylic acid polymer, and an aqueous solvent, wherein said liquid precursor of a glass ionomer cement and said powdered precursor of a glass ionomer cement are present in a ratio of between about 2.5:1 and about 1:1 by weight.

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Elastomeric State Glass Ionomer Cement

Technical Field

The invention relates to an improved, elastomeric state, castable glass ionomer cement, suitable for use as a liner or base in dental restorations, as a replacement for dentine, or for the replacement of enamel.

Background Art

Glass ionomer cements have been available for a number of years, and used for applications such as dentine substitutes, restoration of primary teeth, and luting cements. They are generally supplied in two parts, a powder and a liquid that are mixed together to form a paste that can be applied to surfaces or placed as a restoration. An acid-base reaction occurs that provides a poly(carboxylic) acid component of the liquid with ionic cross-links, and the mixture sets to a hard cement. Traditionally, glass ionomer cements have been slow to cure, lengthening the time required to complete the restoration.

In recent years, light curable glass ionomer cements have been introduced that have improved the convenience to the dentist by shortening the time required to complete the restoration, but in general they rely heavily upon a free radical polymerisation process to generate a cured cement, and no longer rely as heavily upon the acid base reaction that generates fluoride ions and provides good compatibility with dentine. Light curable glass ionomer cements tend to be hard or even glassy materials after light curing that show a lower level of fluoride ion release, and a higher volume shrinkage than classical glass ionomer cements. The present invention relates to a glass ionomer cement that is elastomeric after light curing, and is very close in character to a classical glass ionomer cement.

It has been found that a liquid precursor of a glass ionomer cement, comprising an aqueous solution of polymerisable acid or non-acidic monomers and a poly(carboxylic) acid component, when mixed with a powdered precursor of a glass ionomer cement and subjected to a free radical cross-linking reaction, or an anionic or cationic polymerisation reaction, forms an elastomeric pre-cured material. The water-swollen polymer network of the pre-cured material then reacts with the glass within the powdered glass ionomer cement precursor via an acid-base reaction, providing ionic cross-links which produces a cured glass ionomer cement.

The elastomeric nature of this cavity liner after curing provides some previously unrealised benefits. These advantages include: stress relaxation after curing and allows for good adaptation to the cavity. Furthermore, it reduces the potential for pull-off from the dentine surface when curing the first increment of composite that is placed on the glass ionomer cement. Moreover, it allows for greater ease of handling and use. Further, the glass ionomer cement has the ability to undergo a free radical

polymerisation that is initiated by a catalysed peroxide. This would ensure that the free radical component of the setting process is taken to completion.

Object of the Invention

An object of the invention is to provide a curable glass ionomer cement that is elastomeric after curing, and suitable for use as a liner or base in cavity restoration.

Disclosure of the Invention

According to a first embodiment of the invention, there is provided an elastomeric material obtainable by curing a composition comprising a mixture of a liquid precursor of a glass ionomer cement and a powdered precursor of a glass ionomer cement, said liquid precursor comprising at least one polymerisable monomer present in a range of between 5 to 50% by weight of said liquid precursor of a glass ionomer cement, a carboxylic acid polymer, and an aqueous solvent, wherein said liquid precursor of a glass ionomer cement and said powdered precursor of a glass ionomer cement are in a ratio of between about 2.5:1 and about 1:1 by weight.

According to a second embodiment of the invention, there is provided a method of treating dental caries, comprising applying the elastomeric material in accordance with the first embodiment of the invention as a liner or base for dental or cavity restoration, curing the mixture to form an elastomeric-like material, manipulating the resulting elastomeric material to provide adaptation to the cavity, and allowing an acid-base reaction to proceed to produce a cured glass ionomer cement.

According to a third embodiment of the invention, there is provided an elastomeric material obtainable by curing a composition in accordance with the first embodiment of the invention, wherein the material further comprises a casein phosphopeptide, wherein said liquid precursor of a glass ionomer cement, said powdered precursor of a glass ionomer cement and said casein phosphopeptide are present in a ratio typically from between about 1:1:8 to about 2.5:1:0.0001 by weight.

According to a fourth embodiment of the invention, there is provided a method of treating dental caries comprising applying the elastomeric material in accordance with the third embodiment of the invention as a liner or base for dental or cavity restoration, curing the mixture to form an elastomeric-like material, manipulating the resulting elastomeric material to provide adaptation to the cavity, and allowing an acid-base reaction to proceed to produce a cured glass ionomer cement.

Typically, the elastomeric material is obtainable by curing a composition comprising a mixture of a liquid precursor of a glass ionomer cement, comprising polymerisable acid monomers, a carboxylic acid polymer, a solvent, a free radical initiator and an activator for the free radical initiator, and a powdered precursor of a glass ionomer cement, wherein said liquid precursor of a glass ionomer cement, said powdered precursor of a glass ionomer cement are in a ratio typically from between

about 2.5:1 to about 1:1 by weight, wherein said curing is achieved by a free radical polymerisation reaction.

The preferred ranges for the components of the liquid precursor of the composition in accordance with the first embodiment are as follows:

The polymerisable acid or non-acidic monomer may be present in an amount up to 90% by weight based on the total of the liquid precursor of the glass ionomer cement. Typically, the polymerisable acid or non-acidic monomer is present in a range of between 2 to 50% by weight, more typically in a range between 2 to 45%, 2 to 40%, 2 to 35%, 5 to 35%, 8 to 35%, 10 to 35% or 12 to 35% by weight, and even more typically in a range between 15 to 35% by weight.

Typically, the carboxylic acid polymer may be present in an amount up to 90% by weight based on the total of the liquid precursor of the glass ionomer cement. Typically, the carboxylic acid polymer is present in a range of between 5 to 50% by weight, more typically in a range between 5 to 45%, 5 to 30%, 5 to 25%, 10 to 45%, or 10 to 40% by weight, even more typically in a range between 15 to 40% by weight.

Similarly, the aqueous solvent may be present in an amount up to 80% by weight based on the total of the liquid precursor of the glass ionomer cement. Typically, the aqueous solvent is present in a range of between 10 to 75% by weight, and more typically in a range between 30 to 50% by weight.

Where the elastomeric material is obtained through a free radical polymerisation curing process, a free radical initiator may be present in an amount up to 5% by weight based on the total of the liquid precursor of the glass ionomer cement. Typically, the free radical initiator is present in a range of between 0.01 to 2% by weight, and more typically in a range between 0.1 to 0.5% by weight.

An activator for the free radical initiator may be present in an amount up to 5% by weight, based on the total of the liquid precursor of the glass ionomer cement. Typically, the activator is present in a range of between 0.01 to 2% by weight, and more typically in a range between 0.1 to 0.5% by weight.

The casein phosphopeptide within the composition in accordance with the third embodiment of the invention may be present in an amount up to 80% by weight based on the total of the liquid precursor of the glass ionomer cement. Typically, the casein phosphopeptide is present in a range of between 0.01 to 10% by weight, and more typically in a range between 0.01 to 5% by weight.

Typically, the ratio of the liquid precursor of a glass ionomer cement and the powdered precursor of a glass ionomer cement in accordance with the first embodiment of the invention is about 1.5:1 by weight.

Typically, the ratio of the liquid precursor of a glass ionomer cement, the powdered precursor of a glass ionomer cement and the casein phosphopeptide in accordance with the third embodiment of the invention is about 1.5:1:0.001 by weight.

The liquid precursor of the glass ionomer cement may be comprised of a variety of polymerisable acid or non-acidic monomers, including any acidic or non-acidic monomers that will take part in a free radical polymerisation reaction. Acid monomers are those acids that contain carbon-carbon double bonds. These include methacrylic acid, acrylic acid, itaconic acid, maleic acid, and maleic anhydride. The polymerisable non-acidic monomers may include such monomers as: 2-hydroxy ethyl methacrylate, acrylamide, methacrylamide, or tetrahydrofurfuryl methacrylate. Further, these polymerisable monomers may also be combined with acidic or neutral monomers containing more than one carbon-carbon double bond such as: 1,5-diallyl-2,4-benzene dicarboxylic acid, triethylene glycol dimethacrylate or triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione.

The liquid precursor of the glass ionomer cement may be comprised of a variety of carboxylic acid polymers including any homopolymers with a single type of unit along their side chain, such as poly(acrylic acid) poly(methacrylic acid), and (itaconic acid). The carboxylic acid polymers may also include any copolymers, such as poly(vinyl methyl ether co-maleic acid), poly(methacrylic acid co-acrylic acid), poly(styrene co-acrylic acid co-methacrylic acid). Furthermore, the polymer may have double bonds along the side chain, making the polymer capable of taking part in a free radical reaction.

The liquid precursor of the glass ionomer cement will contain an amount of an aqueous solvent. Suitable aqueous solvents include water, but may also include a mixture such as water and a water miscible liquid such as ethanol or isopropanol.

Both the liquid and powdered precursors of the glass ionomer cement may also contain a free radical initiator such as camphorquinone, azobisisobutyronitrile or riboflavin.

The liquid precursor of the glass ionomer cement may also contain a free radical inhibitor such as butylated hydroxytoluene, hydroquinone and methyl ethyl hydroquinone.

Suitable powdered precursors of the glass ionomer cement include any powder containing any amount of divalent or trivalent metal ions. Examples of these include calcium aluminium fluorosilicate glass, phosphates of zinc and calcium, oxides and hydroxides of calcium, zinc, barium, strontium and aluminium.

The powdered precursor may be comprised of a solid that will generate an acid in the presence of water or an acidic solution. Such a solid may be phosphorous pentoxide, disodium tartrate or disodium maleate.

The powdered precursor may also be comprised of a fluoride as a source of fluoride ions. Suitable examples include sodium fluoride, calcium fluoride, strontium fluoride or sodium aluminium hexafluoride. The liquid precursor may also contain these fluoride sources.

The powdered precursor may also contain a peroxide initiator so that the powder-liquid mixture will undergo a free radical polymerisation in the absence of light, Suitable examples of such a peroxide initiator include: benzoyl peroxide or methyl ethyl ketone peroxide.

When preparing the glass ionomer cement, part, or all of the poly(carboxylic) acid component of the glass ionomer cement may be added to the powdered precursor, so that the dry poly(carboxylic) acid polymer swells or dissolves in the liquid component, when the powdered and liquid precursors of the glass ionomer cement are mixed together.

Typically, the free radical polymerisation reaction is light activated and is brought about by adding to the liquid formulation, a small amount of an initiator such as camphorquinone and an activator such as a tetramethyl amine. A suitable example of such an amine is N,N-3,5-tetramethyl aniline.

Typically, N,N-3,5-tetramethyl aniline may be present in a range of between 0.1% to 5% by weight based on the total of the liquid precursor of the glass ionomer cement. More typically, N,N-3,5-tetramethyl aniline is present in an range of between about 0.1 to about 0.7% by weight, and even more typically in a range between about 0.2 to about 0.5% by weight.

One method of obtaining the elastomeric material of the pre-cured glass ionomer cement is via a free radical polymerisation reaction.

The free radical polymerisation curing reaction is initiated by exposing the admixed liquid and powdered glass ionomer cement precursors to light that contains a significant amount of light at a wavelength at or close to 470nm. The curing time may vary from about 5 to about 80 seconds, but more preferably from about 10 to about 60 seconds. An example of such a light source is provided by the Optilux 401 curing lamp (Demetron Research Corporation).

Alternative methods of obtaining the elastomeric material of the pre-cured glass ionomer cement are to utilise a cationic or anionic polymerisation process. Combinations of Lewis acids and proton donors are important initiators for cationic polymerisation. A suitable combination includes boron trifluoride and water. Anionic polymerisation can be initiated by anionic species by transferring a negative charge to the vinyl double bond, for example potassium amide or a mixture of sodium and naphthalene.

The acid-base reaction that occurs to form a cured glass ionomer cement involves the neutralising of the acid groups in the polymer network by multivalent metal ions such as calcium ions and aluminium ions as provided by the powdered precursor. The acid-base reaction is slow, and the rate of the reaction is limited by the diffusion of metal ions out of the glass powder into the polymer network, and subsequent ionic crosslinking.

The casein phosphopeptide is as disclosed in United States Patent 5,015,628, the disclosure of which is incorporated herein by reference.

The glass ionomer cement may also contain an amount of a heavy metal that would render the material opaque to X-rays, ie radio-opaque. Examples of such heavy metals include barium, bismuth, gold, silver, tin, lead, cadmium, antimony, palladium, platinum, tungsten or iridium. The heavy metals should be in a form sufficiently bound such that undesirable heavy metals are unable to be leached *in vivo*.

Generally, the glass ionomer cement exhibits fracture toughness and flexural modulus values similar to those obtained for classical glass ionomer cements, that is, about 0.4MNm and 6 GPa respectively after 72 hours of curing at ambient temperature.

Best Modes and Other Modes of Carrying Out the Invention

Typically, the preferred compositions of the invention fall within the following ranges, wherein all proportions are calculated by weight:

(a) Liquid Precursor:-	Poly(carboxylic acid)	10 to 55%
	Polymerisable acidic or neutral monomer	5 to 50%
	Solvent	10 to 75%
	Reducing agent	0.1 to 1.0%
	Light activated initiator	0.1 to 1.0%
	Free radical inhibitor	0.1 to 1.0%
(b) Powder Precursor:-	Oxide of tetravalent non-metal	15 to 40%
	Oxide of trivalent metal	25 to 40%
	Oxide of divalent metal	5 to 15%
	Oxide of monovalent metal	2 to 15%
	Phosphorous pentoxide	10 to 25%
	Fluoride ion	8 to 20%
	Free radical initiator	0.01 to 5%
	Powder to provide radio-opacity eg Barium glass	0 to 50%

The powder:liquid ratio is in the range of 1.0:1 to 2.2:1.

A typical formulation for Barium glass may fall within the following range:

Silicone dioxide	5 to 70%
Barium oxide	1 to 50%
Boron oxide	0 to 30%
Aluminium oxide	0 to 25%

Typically, the preferred compositions of the invention, including the casein phosphopeptide, fall within the following ranges:

(a) Liquid Precursor:-	Poly(carboxylic acid)	10 to 55%
	Polymerisable acidic or neutral monomer	5 to 50%
	Solvent	10 to 75%
	Reducing agent	0.1 to 1.0%

	Light activated initiator	0.1 to 1.0%
	Free radical inhibitor	0.01 to 1.0%
(b) Powder Precursor:-	Oxide of tetravalent non-metal	15 to 40%
	Oxide of trivalent metal	25 to 40%
	Oxide of divalent metal	5 to 15%
	Oxide of monovalent metal	2 to 15%
	Phosphorous pentoxide	10 to 25%
	Fluoride ion	8 to 20%
	Free radical initiator	0.01 to 5%
	Powder to provide radio-opacity eg Barium glass	0 to 50%
(c) Casein phosphopeptide		0.01 to 10%

The powder:liquid:casein phosphopeptide ratio is in the range of 1.0:1:8 to 2.5:1:0.0001.

A more preferred composition of the invention falls within the following ranges:

(a) Liquid Precursor:-	Poly(carboxylic acid)	15 to 40%
	Polymerisable acidic or neutral monomer	5 to 35%
	Solvent	15 to 65%
	Reducing agent	0.2 to 0.5%
	Light activated initiator	0.2 to 0.5%
	Free radical inhibitor	0.02 to 0.1%
(b) Powder Precursor:-	Oxide of tetravalent non-metal	22 to 28%
	Oxide of trivalent metal	28 to 34%
	Oxide of divalent metal	7 to 11%
	Oxide of monovalent metal	5 to 10%
	Phosphorous pentoxide	11 to 17%
	Fluoride ion	10 to 16%
	Peroxide initiator	0.05 to 3%
	Powder to provide radio-opacity eg Barium glass	0 to 50%

The powder:liquid ratio is in the range of 1.3:1 to 2.0:1.

A more preferred formulation for Barium glass may fall within the following ranges:

Silicone dioxide	5 to 55%
Barium oxide	1 to 35%
Boron oxide	0 to 15%
Aluminium oxide	0 to 15%

The invention will now be described in greater detail by reference to specific Examples, which should not be construed as limiting on the scope thereof.

Example 1

A novel light curable glass ionomer cement was prepared according to the following:

(a) Liquid Precursor:-	Poly(acrylic acid)	26.0 grams
	Methacrylic acid	16.0 grams
	1,5-diallyl-2,4-benzene dicarboxylic acid	8.0 grams
	Water	50ml
	N,N-3,5-tetramethyl aniline	0.36 grams
	Camphorquinone	0.34 grams
	Butylated hydroxytoluene	0.20 grams
(b) Powder Precursor:-	Calcium aluminium fluorosilicate glass powder	99.8%
	Benzoyl peroxide	0.2%

The powder:liquid ratio is 1.5:1.

The powdered and liquid precursors of the glass ionomer cement are supplied separately. A paste is produced in small quantities as required by introducing small amounts of the liquid precursor to the powdered precursor on a suitably sized plate or mixing receptacle. The liquid and powder precursors are then mixed.

The resulting composition is then cured to an elastomeric state by a free radical polymerisation process. This process is preferably catalysed by light curing. The composition is mixed with an appropriate photoinitiator, either UV or visible light sensitive and an amine accelerator. A free radical inhibitor is added to improve the shelf life of the liquid precursor. An acid-base reaction occurs between the acid groups of the polymer network and the divalent and trivalent metal ions of the powdered precursor to produce a glass ionomer cement.

Example 2

A novel light curable glass ionomer cement was prepared according to the following:

(a) Liquid Precursor:-	Poly(acrylic acid)	18.0 grams
	Methacrylic acid	16.0 grams
	1,5-diallyl-2,4-benzene dicarboxylic acid	16.0 grams
	Water	50ml
	N,N-3,5-tetramethyl aniline	0.36 grams
	Camphorquinone	0.34 grams
	Butylated hydroxytoluene	0.02 grams
(b) Powder Precursor:-	Calcium aluminium fluorosilicate glass powder	99.8%

	Benzoyl peroxide	0.2%

The powder:liquid ratio is 1.5:1.

The glass ionomer cement is produced in accordance with the method described in Example 1.

Example 3

A novel light curable glass ionomer cement was prepared according to the following:

(a) Liquid Precursor:-	Poly(acrylic acid)	18.0 grams
	Methacrylic acid	20.0 grams
	1,5-diallyl-2,4-benzene dicarboxylic acid	12.0 grams
	Water	50ml
	N,N-3,5-tetramethyl aniline	0.36 grams
	Camphorquinone	0.34 grams
	Butylated hydroxytoluene	0.02 grams
(b) Powder Precursor:-	Calcium aluminium fluorosilicate glass powder	79.8%
	Barium glass	20.0%
	Benzoyl peroxide	0.2%
(c) Casein Phosphopeptide		2%

The powder:liquid:casein phosphopeptide ratio is 1.5:1:0.001.

The glass ionomer cement is produced in accordance with the method described in Example 1.

Industrial Applicability

The glass ionomer cement of the invention can be used in place of amalgam in dental restorations.

Claims

1. An elastomeric material obtainable by curing a composition comprising a mixture of a liquid precursor of a glass ionomer cement and a powdered precursor of a glass ionomer cement, said liquid precursor comprising at least one polymerisable monomer present in a range of between 2 to 50% by weight of said liquid precursor of a glass ionomer cement, a carboxylic acid polymer, and an aqueous solvent, wherein said liquid precursor of a glass ionomer cement and said powdered precursor of a glass ionomer cement are present in a ratio of between about 2.5:1 and about 1:1 by weight.

2. The elastomeric material according to claim 1, wherein said polymerisable monomer is present in a range of between 15 to 35% by weight of said liquid precursor of a glass ionomer cement.

3. The elastomeric material according to claim 1, wherein said liquid precursor of a glass ionomer cement and said powdered precursor of a glass ionomer cement are present in a ratio of about 1.5:1 by weight.

4. The elastomeric material according to claim 1, further comprising a casein phosphopeptide.

5. The elastomeric material according to claim 4, wherein said liquid precursor of a glass ionomer cement, said powdered precursor of a glass ionomer cement and said casein phosphopeptide are present in a ratio of between about 1:1:8 and about 2.5:1:0.0001 by weight.

6. The elastomeric material according to claim 4, wherein said liquid precursor of a glass ionomer cement, said powdered precursor of a glass ionomer cement and said casein phosphopeptide are present in a ratio of about 1.5:1:0.001 by weight.

7. The elastomeric material according to claim 1, wherein said liquid precursor of a glass ionomer cement further comprises a free radical initiator and an activator for said free radical initiator.

8. The elastomeric material according to claim 1, wherein said curing is achieved by a free radical polymerisation reaction.

9. The elastomeric material according to claim 8, wherein said free radical polymerisation reaction is light activated.

10. The elastomeric material according to claim 9, wherein said light has a wavelength of about 470nm.

11. The elastomeric material according to claim 1, wherein said curing is achieved by a cationic polymerisation process.

12. The elastomeric material according to claim 1, wherein said curing is achieved by a anionic polymerisation process.

13. The elastomeric material according to claim 1, wherein the liquid precursor of a glass ionomer cement comprises at least one acid monomer that is capable of taking part in a free radical polymerisation reaction.

14. The elastomeric material according to claim 13, wherein said acid monomer is selected from the group consisting of: methacrylic acid, acrylic acid, itaconic acid, maleic acid, 1,5-diallyl-2,4-benzene dicarboxylic acid and maleic anhydride.

15. The elastomeric material according to claim 1, wherein the liquid precursor of a glass ionomer cement comprises at least one non-acidic monomer that is capable of taking part in a free radical polymerisation reaction.

16. The elastomeric material according to claim 15, wherein said non-acidic monomer is selected from the group consisting of: 2-hydroxy ethyl methacrylate, acrylamide, methacrylamide, triethylene glycol dimethacrylate, triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione and tetrahydrofurfuryl methacrylate.

17. The elastomeric material according to claim 7, wherein said activator is an amine.

18. The elastomeric material according to claim 17, wherein said amine is N,N-3,5-tetramethyl aniline.

19. The elastomeric material according to claim 1, wherein said liquid precursor of a glass ionomer cement includes a free radical inhibitor.

20. The elastomeric material according to claim 1, wherein said carboxylic acid polymer is a homopolymer.

21. The elastomeric material according to claim 20, wherein said carboxylic acid polymer is selected from the group consisting of: poly(acrylic acid), poly(methacrylic acid), and poly(itaconic acid).

22. The elastomeric material according to claim 1, wherein said carboxylic acid polymer is a copolymer.

23. The elastomeric material according to claim 22, wherein said carboxylic acid polymer is selected from the group consisting of: poly(vinyl methyl ether co-maleic acid), poly(methacrylic acid co-acrylic acid) and poly(styrene co-acrylic acid co-methacrylic acid).

24. The elastomeric material according to claim 1, wherein said aqueous solvent is water.

25. The elastomeric material according to claim 1, wherein said aqueous solvent is a mixture of water with ethanol or with isopropanol.

26. The elastomeric material according to claim 1, wherein said powdered precursor of a glass ionomer cement includes divalent or trivalent metal ions.

27. The elastomeric material according to claim 26, wherein said powdered precursor of a glass ionomer cement is selected from the group consisting of: calcium aluminium fluorosilicate glass, phosphates of zinc and calcium, or oxides and hydroxides of calcium, zinc, barium, strontium and aluminium.

28. The elastomeric material according to claim 1, wherein said powdered precursor of a glass ionomer cement comprises a solid that will generate an acid in the presence of water or an acidic solution.

29. The elastomeric material according to claim 28, wherein said powdered precursor of a glass ionomer cement is selected from the group consisting of: phosphorus pentoxide, disodium tartrate and disodium maleate.

30. The elastomeric material according to claim 1, wherein said powdered precursor of a glass ionomer cement comprises a fluoride.

31. The elastomeric material according to claim 30, wherein said fluoride is selected from the group consisting of: sodium fluoride, calcium fluoride, strontium fluoride and sodium aluminium hexafluoride.

32. The elastomeric material according to claim 1, wherein said powdered precursor of a glass ionomer cement further comprises a peroxide initiator.

33. The elastomeric material according to claim 1, further comprising an amount of heavy metal sufficient to render the cement substantially radio-opaque.

34. The elastomeric material according to claim 33, wherein said heavy metal is selected from the group consisting of: barium, bismuth, gold, silver, tin, lead, cadmium, antimony, palladium, platinum, tungsten and iridium.

35. A method of treating dental caries, comprising applying an elastomeric material according to claim 1, as a liner or base for dental or cavity restoration, curing the mixture to form an elastomeric-like material, manipulating the resulting elastomeric material to provide adaptation to the cavity, and allowing an acid-base reaction to proceed to produce a cured glass ionomer cement.

36. A method of treating dental caries, comprising applying an elastomeric material according to claim 4, as a liner or base for dental or cavity restoration, curing the mixture to form an elastomeric-like material, manipulating the resulting elastomeric material to provide adaptation to the cavity, and allowing an acid-base reaction to proceed to produce a cured glass ionomer cement.

37. The method of claim 35 or 36, wherein said curing is achieved by a free radical polymerisation reaction.

38. The method of claim 35 or 36, wherein said curing is achieved by a cationic polymerisation process.

39. The method of claim 35 or 36, wherein said curing is achieved by a anionic polymerisation process.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/AU 97/00208

A. CLASSIFICATION OF SUBJECT MATTER

Int Cl[6]: C08F 265/02, 267/02, A61K 6/083

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)
IPC C08F 265/02, 267/02, A61K 6/083

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPAT: DENT: TOOTH: TEETH: GLASS IONOMER

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 329268 A (KERR MANUFACTURING CORPORATION) 23 August 1989 page 3 line 8 - page 4 line 49, examples and claims	1-39
X	GB 2291428 A (KABUSHIKI KAISHA GC) 24 January 1996 claims	1-39
X	AU 46717/89 (627252)B (G-C SHIKA KOGYO KABUSHIKI KAISHA) 21 June 1990 page 3 line 18 - page 14 line 27, claims	1-39

[X] Further documents are listed in the continuation of Box C

[X] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"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)

"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

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 May 1997	7 MAY 1997
Name and mailing address of the ISA/AU AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No.: (06) 285 3929	Authorized officer **S.CHEW** Telephone No.: (06) 283 2248

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/AU 97/00208

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	GB 2297692A (KABUSHIKI KAISHA GC) 14 August 1996 page 20 line 25 - page 22 line 15, claims	1-39
A	WO 88/01859 A (DEN MAT CORPORATION) 24 March 1988 entire document	1-39
A	DE 3934803 A (VOCO CHEMIE GmbH) 25 April 1991 entire document	1-39
A	DT 2651316 A (G-C DENTAL INDUSTRIAL CORP) 25 August 1977 entire document	1-39

INTERNATIONAL SEARCH REPORT
Information on patent family members

International Application No.
PCT/AU 97/00208

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
AU	46717/89	BE	1002916	CH	680340	DE	3941629
		FR	2640503	GB	2228001	JP	2164807
		NL	8903089	SE	8904240	US	5063257
WO	8801859	AU	80388/87	EP	324782	US	4738722
GB	2291428	DE	19526224	GB	2291428	JP	8026925
		US	520725				
EP	329268	AU	27737/89	BR	8900112	EP	329268
		JP	1308855				
GB	2297692	DE	19605272	JP	8217612		
DE	3934803						
DT	2651316						

END OF ANNEX