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(54) **Dental restorative compounds**  
Verbindungen für Zahnersatzteile  
Composition de restauration dentaire

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(56) References cited:  
**WO-A-01/95862 US-A- 5 859 089**

- **PATENT ABSTRACTS OF JAPAN vol. 1995, no. 10, 30 November 1995 (1995-11-30) & JP 07 179401 A (TOKUYAMA CORP), 18 July 1995 (1995-07-18) -& JP 07 179401 A (TOKUYAMA CORP) 18 July 1995 (1995-07-18)**
- **DATABASE WPI Section Ch, Week 199310 Derwent Publications Ltd., London, GB; Class A12, AN 1993-080298 XP002265966 & JP 05 025016 A (TOKUYAMA SODA KK), 2 February 1993 (1993-02-02) -& JP 05 025016 A (TOKUYAMA SODA KK) 2 February 1993 (1993-02-02)**

Remarks:

The file contains technical information submitted after the application was filed and not included in this specification

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## Description

[0001] The invention relates generally to a dental restorative composition comprising a tri-functional diluent monomer that results in reduced polymerization shrinkage, adequate viscosity, and good mechanical properties.

[0002] Resin based dental restorative materials are becoming the material of choice by dentists and patients due to desirable aesthetic properties. However, one serious drawback associated with resin based restorative material is significant polymerization shrinkage when the material undergoes the setting reaction. Polymerization shrinkage, in turn, causes gap formation between the restoration and tooth, leading to microleakage, secondary caries or loss of restoration. Polymerization shrinkage is a result of converting the C=C double bonds of low molecular weight monomers to C-C single bonds of crosslinked polymers during the setting reaction.

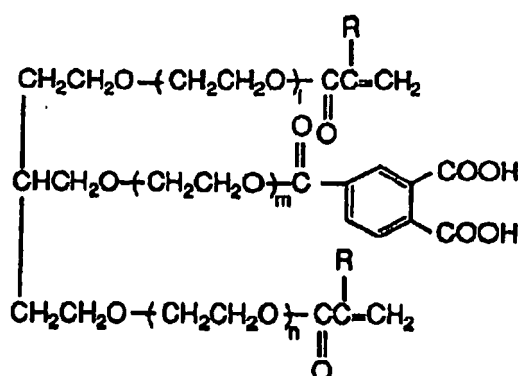
[0003] Usually, a low viscosity di-functional monomer such as TEGDMA (triethylene glycol dimethacrylate) or HDDA (1,6-hexanediol diacrylate) is added as a diluent to a viscous resin such as Bis-GMA (2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)-phenyl]-propane)) to form a resin mixture so that reinforcing fillers can be more easily incorporated into the resins. However, because those low viscosity di-functional monomers have a rather low molecular weight, significant polymerization shrinkage results when compositions containing those diluent monomers are polymerized.

[0004] Various attempts have been made to utilize liquid crystal monomers to reduce polymerization shrinkage (Mol. Cryst. Liq. Cryst., 11, p385, 1970; J. Polym. Sci., A-1, 9, p1893, 1971). Most nematic liquid crystalline monomers do not polymerize efficiently and, as a result, a low degree of conversion is obtained. Qian and Litt in Contemporary Topics in Polymer Science, (Vol. 7, p361, 1992) disclosed highly smectic liquid crystal diacrylate monomers based on biphenyl mesogen; very low shrinkage was obtained. Anderson et al. (Macromol. Symp. p339, 1994) disclosed smectic and nematic liquid crystal divinyl ether monomers based on bishydroxybenzoate mesogen. However, most liquid crystalline monomers have a high liquid crystal transition temperature, high viscosity, and/or low translucency, and thus are not suitable for dental use.

[0005] Another approach to reduce polymerization shrinkage is to increase the molecular weight of the monomer and make the monomer molecule larger. However, when higher molecular weight analogues of TEGDMA, such as PEGDMA (polyethylene glycol dimethacrylate) are used, a significant reduction in mechanical strength is observed due to reduced crosslinking density of the resin matrix. Most high molecular weight mono-functional and di-functional diluents would encounter the same problem. U.S. Patent No. 6,030,606 disclosed the use of a highly ethoxylated bisphenol A dimethacrylate (6 moles of ethylene oxide per molecule) for incorporation in dental resin mixtures for reducing polymerization shrinkage.

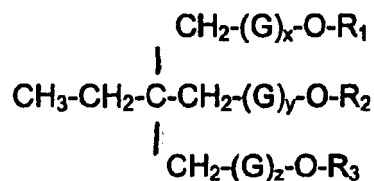
[0006] WO 01/95862 discloses a low shrinking polymerizable dental material, includes a mixture of a polymerizable di- or poly(meth)acrylate, an alkoxyated bisphenol dimethacrylate, a polymerizable monomer, a polymerisation initiator and/or sensitizer, a stabilizer and a filler in a content of 70 to 85 per cent. The volumetric shrinkage during polymerization is less than 2.0 Vol-%.

[0007] JP 07-179401 discloses a composition for use as an adhesive for restorations comprising the acid group-containing (meth)acrylate monomer of the formula below



[0008] The present invention provides

(a) a first alkoxyated and trifunctional monomer of the general formula



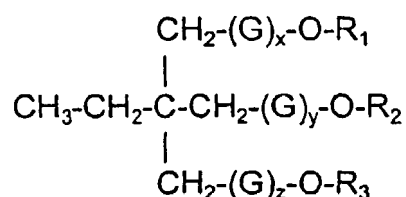
wherein G is an alkylene oxide unit, and  $6 \leq x + y + z \leq 30$ , and  $R_1$ ,  $R_2$ , and  $R_3$  are ethylenically unsaturated groups, (b) a second monomer which can co-polymerise with the first monomer comprising at least one ethylenically unsaturated group, the second monomer selected from at least one of hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, hydroxybutyl (meth)acrylate, glycerol di(meth)acrylate, glycerol mono(meth)acrylate, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, hexyl (meth)acrylate, octyl (meth)acrylate, lauryl (meth)acrylate, decyl (meth)acrylate, tridecyl (meth)acrylate; 2-ethoxyethyl (meth)acrylate, 2-ethoxy-2-ethoxyethyl (meth)acrylate, ethyleneglycol di(meth)acrylate, diethyleneglycol di(meth)acrylate, triethyleneglycol di(meth)acrylate, tetraethyleneglycol di(meth)acrylate, polyethyleneglycol mono-(meth)acrylate, polyethyleneglycol di-(meth)acrylate, polypropyleneglycol mono-(meth)acrylate, polypropyleneglycol di-(meth)acrylate, polytetramethyleneglycol mono-(meth)acrylate, polytetramethyleneglycol di-(meth)acrylate, hexanediol di(meth)acrylate, trimethyloxypropane tri(meth)acrylate, UDMA, Bis-GMA, EBPADMA-n, tetrahydrofurfuryl (meth)acrylate, or TEGDMA or a mixture thereof, and (c) a polymerization initiator.

**[0009]** The invention is directed to a dental restorative composition comprising a first monomer having three ethylenically unsaturated groups, a second monomer having at least one ethylenically unsaturated group, and a free radical polymerization initiator system. A filler is optional. The first monomer is alkoxyated and tri-functional and, when used as a diluent, results in a resin blend and dental restorative composition that has significantly reduced shrinkage and excellent mechanical properties. The composition may be used as a dental filling material, a dental cement, a dental liner/base, or a dental adhesive.

#### DETAILED DESCRIPTION

**[0010]** Disclosed are highly alkoxyated tri-functional monomers useful as a low viscosity diluent monomer in a photo-curable (with a photo-initiator) and/or self-curable (with a redox initiator) dental composition that resulted in significantly lower polymerization shrinkage. The mechanical strength of the resulting restorative material was not compromised. The restorative composition incorporating the tri-functional monomers can be used as a dental filling material, cement, liner/base, or adhesive.

**[0011]** More specifically, the dental restorative composition comprises a first monomer with three ethylenically unsaturated groups of the following structure:



wherein G is a linear or branched alkylene oxide unit, and  $R_1$ ,  $R_2$ , and  $R_3$  are ethylenically unsaturated groups. When the tri-functional monomer is used as a diluent, the resulting resin blend and subsequent dental restorative composition had significantly reduced shrinkage and excellent mechanical properties.

**[0012]** The dental restorative composition also includes a second monomer having at least one ethylenically unsaturated functional group, and a curing initiator system, either a photo-initiator and/or a redox initiator system as a free-radical polymerization initiator system. A filler may optionally be included.

**[0013]** The highly alkoxyated tri-functional monomer, also referred to as component (a), has three ethylenically unsaturated groups  $R_1$ ,  $R_2$ , and  $R_3$ , which may be the same or different. In one embodiment  $R_1$ ,  $R_2$ , and  $R_3$  are independently selected from the group consisting of



material, the concentration range may be 30-95%.

**[0017]** The curing initiator, also referred to as component (d), is a free-radical polymerization initiator, either a photo-initiator and/or a redox initiator. Examples of photo-initiators include benzoin, benzoin ethers and esters, 2,2-diethoxy acetophenone, diketone compounds, bisacylphosphine oxide, diaryliodonium salt, triarylsulfonium salt and a mixture of photo-initiators. Additionally, an activator such as a tertiary amine can be used together with the above photo-initiators to enhance the curing efficiency. In embodiments, the photo-initiator systems include camphoroquinone and a tertiary amine such as ethyl 4-(N,N-dimethylamino) benzoate, 2-(ethylhexyl)-4-(N,N-dimethylamino) benzoate, and N,N-dimethylaminoethyl methacrylate.

**[0018]** A redox initiator system comprises at least one reducing agent and at least one oxidizing agent. The reducing agent may be a tertiary amine, or an organic compound containing the  $-SO_2M$  (M is H or alkali metal ion) group, such as a sulfinic acid or an alkali metal sulfinate. In embodiments, the reducing agent may be N,N-dihydroxyethyl p-toluidine, N,N-dimethyl p-toluidine, N,N-dimethylaminophenylethyl alcohol, N,N-dimethylaminophenylacetic acid, benzenesulfinic acid, toluenesulfinic acid, sodium benzenesulfinate, potassium benzenesulfinate, sodium toluenesulfinate, and/or potassium toluenesulfinate. The oxidizing agent may be a peroxide, such as benzoyl peroxide, hydrogen peroxide, di-t-butyl peroxide, and/or t-butyl hydrogen peroxide. The photo-initiator and redox initiator can be used alone or together. A photo-initiator is often used in a single part light-cure only system. A redox initiator is used in a two-part self-cure (i.e. curing without activation of light) system with each part containing one component (either the oxidizing agent or the reducing agent) of the redox initiator system. The photo-initiator can be used in combination with the redox initiator system to make the system dual-cure, i.e. both light-cure and self-cure. In embodiments, the concentration of the initiators is in the range of 0.01% to 5.0% by weight, or in the range of 0.05% to 3.0% by weight.

**[0019]** Other ingredient can also be incorporated in the inventive composition, such as colorants, stabilizers, UV absorbers, and/or antimicrobial additives. Colorants are used to achieve a desired shade, and can be inorganic pigments or organic dyes. Stabilizers are polymerization inhibitors to improve the shelf stability of the restorative material. Most commonly used stabilizers include 2,6-di-(tert-butyl)-4-methylphenol (BHT) and 4-methoxyphenol (MEHQ). UV absorbers are used to improve the color stability of the restorative material upon exposure to UV light. An example of UV absorber is 2-hydroxy-4-methoxybenzophenone (UV-9).

**[0020]** The inventive resins are useful in formulating restorative materials such as a filling material, a cement, a base/liner, or an adhesive. They are useful in restorative filling materials where a reduction in polymerization shrinkage is most important in minimizing interfacial polymerization shrinkage stress and gap formation. The restorative material can be a purely resin-based composite, or a hybrid material such as a resin-ionomer (RI) or resin-modified glass-ionomer (RMGI). RMGI is a hybrid material that contains a minimum of following ingredients: acidic monomer or polymer, water, monomer with at least one ethylenically unsaturated group, and an ion-leachable filler that can undergo a setting reaction with the acidic monomer or polymer, and a polymerization initiator. The acidic monomer or polymer may contain at least one ethylenically unsaturated group. The curing initiator may be a photo-initiator, a redox initiator, or a combination of both. The inventive tri-functional resins may be useful in a RMGI cement or restorative because they are water dispersible or soluble, especially when other hydrophilic monomers such as hydroxyethyl methacrylate (HEMA) or glycerol dimethacrylate (GDM) are present. Besides reduced curing shrinkage, incorporation of the inventive resins in RMGI improves other mechanical and physical properties due to better network formation during polymerization because of their tri-functionality.

**[0021]** The restorative composition can also incorporate a solvent, especially when an adhesive or cement composition is formulated. Useful solvents include water, methanol, ethanol, isopropanol, acetone, and MEK (methyl ethyl ketone).

**[0022]** The invention also includes a method for preparing the inventive composition, using the composition to restore the diseased tooth, and hardening the composition inside the patient's mouth.

**[0023]** The following examples illustrate how current invention is applied and should not limit the scope of the invention.

## Testing Methods

### Compressive Strength (CS) Test

**[0024]** Specimens were prepared by condensing the paste into a stainless-steel mold with a dimension of 4 mm (diameter) x 3 mm (height), and then photo-curing the paste with a Demetron Optilux 401 curing light (Kerr Corp., Orange, CA) for 30 seconds from each side. The cured disk was removed from the mold and conditioned in 37°C water for 24 hours before subjecting to mechanical testing on an Instron Universal Tester (Model 4202) in compression mode with a crosshead speed of 0.50 mm/minute. The peak load at which the specimen breaks is used to calculate the compressive strength, expressed in MPa unit. Six specimens were tested for each formula.

Diametral Tensile Strength (DTS) Test

[0025] Specimens were prepared by condensing the paste into a stainless-steel mold with a dimension of 6 mm (diameter) × 3 mm (height), and then photo-curing the paste with a Demetron Optilux 401 curing light (Kerr Corp.) for 30 seconds from each side. The cured disk was removed from the mold and conditioned in 37°C water for 24 hours before subjecting to mechanical testing on an Instron Universal Tester (Model 4202) in compression mode with a cross-head speed of 10 mm/minute. The load was applied in the diameter direction in compression mode. The peak load at which the specimen breaks is used to calculate the compressive strength expressed in MPa unit. Six specimens were tested for each formula.

Flexural Strength (FS) and Young's Modulus (E) Tests

[0026] FS and E were measured from the same flexural test according to ISO 4049 standard. The specimens were prepared by condensing the paste into a stainless-steel mold with dimensions of 2 mm × 2 mm × 25 mm, and then photo-cured from both sides. The cured disk was removed from the mold and conditioned in 37°C water for 24 hours before subjecting to mechanical testing on an Instron Universal Tester (Model 4202) in 3-point bending mode with a crosshead speed of 0.5 mm/minute. The peak load at which the specimen breaks is used to calculate the FS, expressed in MPa units. E was obtained from the slope of stress-strain curve in the initial linear region. Six specimens were tested for each formula.

Volumetric polymerization shrinkage (VPS)

[0027] VPS was calculated based on the measured densities of the material before and after light-curing with a Demetron 401 curing light for 60 seconds. The density was measured using buoyancy method in deionized water.

**Examples**

[0028] One-part light-curable composite resin filling materials were formulated and tested in the following examples. Other configurations are readily obtained by one skilled in the art, by incorporating different curing initiators (photo-initiator and/or redox initiator), filler type (reactive filler and/or non-reactive filler with acid), and viscosity (varying filler concentration, solvent). These may included light-cure vs. self-cure or dual-cure; one-part vs. two-part; filling material vs. cement, liner/base, or adhesive; composite resin vs. hybrid material such as resin-ionomer or resin-modified glass-ionomer, etc.

[0029] In all the following examples for making the one-part light-cure composite paste (as a filling material), a homogeneous unfilled resin mixture (A, B, C, D, E, F, or G) was made first by mixing all resins with initiators and additives that are soluble in the resin mixture. The resin mixture (A, B, C, D, E, F, or G) was then further blended together with surface-treated fillers including fumed silica (TS530 and OX-50) and a barium glass filler to make a composite paste (A-1, B-1, C-1, D-1, E-1, F-1, or G-1). Paste A-1 was made with resin mixture A, Paste B-1 was made with resin mixture B, and likewise. Unless otherwise indicated, all parts and percentages are by weight in all examples.

[0030] In the examples the following materials were used:

A-174:  $\gamma$ -methacryloyloxypropyltrimethoxysilane

Barium Glass filler: Bariumaluminoborosilicate filler that has an mean particle size of 1.0 micron and the following composition mole%: SiO<sub>2</sub> (67%), BaO (16.4%), B<sub>2</sub>O<sub>3</sub> (10%), Al<sub>2</sub>O<sub>3</sub> (6.6%)

BHT: 2,6-di-(*tert*-butyl)-4-methylphenol

Bis-GMA: 2,2-bis[4-(2-hydroxy-3-methacryloylpropoxy)-phenyl]-propane

CQ: camphoroquinone

EDMAB: ethyl-4-(N,N-dimethylamino) benzoate

EBPADMA-4: ethoxylated bisphenol A dimethacrylate with 4 moles of ethylene oxide

TMPT-A-EO-6: highly ethoxylated trimethylolpropane triacrylate with 6 moles of ethylene oxide

TMPT-A-EO-9: highly ethoxylated trimethylolpropane triacrylate with 9 moles of ethylene oxide

TMPT-A-EO-15: highly ethoxylated trimethylolpropane triacrylate with 15 moles of ethylene oxide

OX-50: fumed silica or colloidal silica sold by Degussa

TEGDMA: triethyleneglycol dimethacrylate

TS-530: surface treated fumed silica or colloidal silica sold by Cabot Corp.

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Table I. Resin Mixture Formulas							
Resin Mixture	A	B	C	D	E	F	G
BISGMA	4.1	4.1	4.1	4.1	4.1	4.1	4.1
EBPADMA-4	65	65	65	65	65	65	65
TEGDMA	30				5		
TMPT-A-EO-6		30				10	10
TMPT-A-EO-9			30		25	20	
TMPT-A-EO-15				30			20
EDMAB	0.64	0.64	0.64	0.64	0.64	0.64	0.64
CQ	0.20	0.20	0.20	0.20	0.20	0.20	0.20
BHT	0.06	0.06	0.06	0.06	0.06	0.06	0.06

Table II. Composite Paste Formulas Using Resin Mixtures A-G of Table I							
Composite Paste	A-1	B-1	C-1	D-1	E-1	F-1	G-1
Resin Mixture (A-G)	23 (A)	23 (B)	23 (C)	23 (D)	23 (E)	23 (F)	23 (G)
TS-530	3	3	3	3	3	3	3
OX-50*	3.52	3.52	3.52	3.52	3.52	3.52	3.52
Barium Glass*	70.48	70.48	70.48	70.48	70.48	70.48	70.48
* OX-50 and Barium Glass are surface-treated with gamma-methacryloyloxypropyltrimethoxysilane							

Table III. Physical Properties of Composite Pastes							
Composite Paste	A-1	B-1	C-1	D-1	E-1	F-1	G-1
CS (MPa)	405 (47)**	441 (26)	402 (21)	417 (15)	442 (13)	429 (19)	405 (31)
DTS (MPa)	44.3 (6.9)	53.3 (5.6)	53.9 (9.0)	50.1 (9.2)	49.2 (8.3)	49.7 (4.6)	59.8 (5.5)
FS (MPa)	137.2 (9.3)	138.5 (6.7)	124.3 (3.1)	118.4 (6.5)	131.0 (8.7)	124.6 (11.1)	128.4 (4.8)
E (GPa)	11.4 (0.6)	10.0 (0.5)	9.0 (0.5)	8.3 (0.1)	9.9 (0.6)	9.6 (0.6)	9.2 (0.9)
VPS (%)	3.06 (0.08)	2.63 (0.07)	2.58 (0.02)	2.57 (0.02)	2.60 (0.03)	2.63 (0.04)	2.56 (0.03)
** The number in parenthesis is standard deviation							

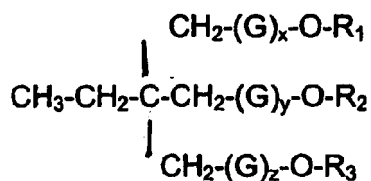
**[0031]** TEGDMA is currently being used as a diluent by many dental manufacturers for making composite materials. For comparison purposes, formula A-1 was made using TEGDMA as a diluent. Formulas B-1 to G-1 used various inventive tri-functional diluents, or a combination of tri-functional diluents, replacing TEGDMA. The composite materials (formulas B-1 to G-1) using the inventive tri-functional diluents all had significantly reduced VPS compared to the reference formula A-1 using TEGDMA as a diluent. The mechanical strengths (CS, DTS, and FS) of formulas using the inventive tri-functional diluents are comparable or superior to the reference formula using TEGDMA. Polymerization shrinkage stress is proportional to the product of VPS and E (E measures the rigidity of the material).

Composite materials (formulas B-1 to G-1) using the inventive tri-functional diluents all had reduced E compared to the reference formula A-1 using TEGDMA as a diluent. Therefore the combination of reduced VPS and reduced E would lead to an even greater reduction in polymerization shrinkage stress for formulas B-1 to G-1 that use tri-functional diluents. This would significantly reduce the stress exerted at the restoration-tooth interface and minimize gap formation.

Claims

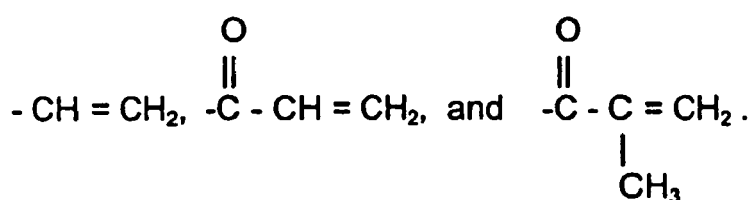
1. A dental restorative composition comprising

(a) a first alkoxyated and trifunctional monomer of the general formula



wherein G is an alkylene oxide unit, and  $6 \leq x + y + z \leq 30$ , and  $R_3$  are ethylenically unsaturated groups,  
 (b) a second monomer which can co-polymerise with the first monomer comprising at least one ethylenically unsaturated group, the second monomer selected from at least one of hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, hydroxybutyl (meth)acrylate, glycerol di(meth)acrylate, glycerol mono(meth)acrylate, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, hexyl (meth)acrylate, octyl (meth)acrylate, lauryl (meth)acrylate, decyl (meth)acrylate, tridecyl (meth)acrylate; 2-ethoxyethyl (meth)acrylate, 2-ethoxy-2-ethoxyethyl (meth)acrylate, ethyleneglycol di(meth)acrylate, diethyleneglycol di(meth)acrylate, triethyleneglycol di(meth)acrylate, tetraethyleneglycol di(meth)acrylate, polyethyleneglycol mono-(meth)acrylate, polyethyleneglycol di-(meth)acrylate, polypropyleneglycol mono-(meth)acrylate, polypropyleneglycol di-(meth)acrylate, polytetramethyleneglycol mono-(meth)acrylate, polytetramethyleneglycol di-(meth)acrylate, hexanediol di(meth)acrylate, trimethyloxypropane tri(meth)acrylate, UDMA, Bis-GMA, EBPADMA-n, tetrahydrofurfuryl (meth)acrylate, or TEGDMA or a mixture thereof, and  
 (c) a polymerization initiator.

2. The dental restorative composition of claim 1 wherein  $R_1$ ,  $R_2$ , and  $R_3$  are selected from the group consisting of



3. The dental restorative composition of any preceding claim wherein  $x + y + z$  is in the range of 3 to 15.
4. The dental restorative composition of claim 1 wherein the first monomer comprises a combination of at least two different tri-functional monomers and the mean  $(x+y+z)$  is  $\geq 3$  and  $\leq 30$ .
5. The dental restorative composition of claim 1 wherein the first monomer comprises a combination of at least two different tri-functional monomers and the mean  $(x+y+z)$  is in the range of 3 to 15.
6. The dental restorative composition of any preceding claim wherein G is  $-\text{OC}_n\text{H}_{2n}-$  and n is in the range between 1 and 12.

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7. The dental restorative composition of any preceding claim wherein G is a linear or branched alkylene oxide unit.
8. The dental restorative composition of any preceding claim further comprising a finely divided filler.
- 5 9. The dental restorative composition of claim 8 wherein the filler is selected from the group consisting of inorganic metal, salt, oxide, silicate, aluminosilicate, aluminoborosilicate, fluoroaluminosilicate, colloidal silica, precipitated silica, polymeric filler, polymerized composite filler with inorganic particles, and combinations thereof.
- 10 10. The dental restorative composition of claim 8 wherein the filler is selected from the group consisting of bariumaluminosilicate, bariumaluminoborosilicate, strontiumaluminosilicate, zincaluminosilicate, bariumaluminumfluorosilicate, strontiumaluminumfluorosilicate, fumed silica, and combinations thereof.
- 15 11. The dental restorative composition of any one of claims 8 to 10 wherein the filler has a mean particle size less than 15  $\mu\text{m}$ .
12. The dental restorative composition of any one of claims 8 to 10 wherein the filler has a mean particle size less than 5  $\mu\text{m}$ .
- 20 13. The dental restorative composition of any one of claims 8 to 10 wherein the filler has a mean particle size less than 2  $\mu\text{m}$ .
14. The dental restorative composition of any one of claims 8 to 13 wherein the filler comprises a nano-particle filler.
- 25 15. The dental restorative composition of any one of claims 8 to 14 wherein the filler has a mean particle size in the range of 5 nm to 200 nm.
16. The dental restorative composition of any one of claims 8 to 15 wherein the filler is surface treated or surface coated with a coupling agent.
- 30 17. The dental restorative composition of claim 16 wherein the coupling agent is  $\gamma$ -methacryloyloxypropyltrimethoxysilane.
18. The dental restorative composition of any preceding claim wherein the polymerization initiator is selected from the group consisting of a photo initiator system, a redox initiator system, and combinations thereof.
- 35 19. The dental restorative composition of any preceding claim wherein the composition is a one-part light-cure composition having a photo-initiator system.
20. The dental restorative composition of any one of claims 1 to 18 wherein the composition is a two-part self-cure composition having a redox initiator system.
- 40 21. The dental restorative composition of any one of claims 1 to 18 wherein the composition is a two-part dual-cure composition having a combined photo-initiator and redox initiator system.
- 45 22. The dental restorative composition of any one of claims 18, 19 or 21 wherein the photo-initiator system comprises a photo-sensitizer and an activator.
23. The dental restorative composition of claim 22 wherein the photo-sensitizer is camphorquinone.
- 50 24. The dental restorative composition of either claim 22 or claim 23 wherein the activator is a tertiary amine.
25. The dental restorative composition of any one of claims 18, 20 or 21 wherein the redox initiator system comprises an oxidizing agent and a reducing agent.
- 55 26. The dental restorative composition of claim 25 wherein the oxidizing agent is a peroxide.
27. The dental restorative composition of either claim 25 or claim 26 wherein the reducing agent is selected from the group consisting of a tertiary amine, a sulfinic acid, an alkali metal sulfinic acid, and combinations thereof.

28. The dental restorative composition of any preceding claim further comprising a solvent selected from the group consisting of water, acetone, methanol, ethanol, isopropanol, and combinations thereof.

29. The dental restorative composition of any preceding claim further comprising a stabilizer.

30. The dental restorative composition of any preceding claim further comprising a UV stabilizer.

31. The dental restorative composition of any preceding claim wherein the composition is selected from the group consisting of resin composite, a resin-ionomer, and a resin-modified glass-ionomer.

32. The dental restorative composition of any preceding claim used as a filling material, a cement, a liner, a base, an adhesive, or a combination thereof.

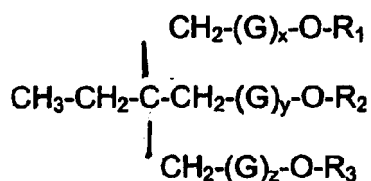
33. The dental restorative composition of any one of claims 8 to 31 as dependent on claim 1 wherein G is selected from the group consisting of ethylene oxide, n-propylene oxide, isopropylene oxide, n-butylene oxide, and combinations thereof,  $3 \leq x + y + z \leq 20$ , and  $R_1$ ,  $R_2$  and  $R_3$  are independently selected from the group consisting of acrylate and methacrylate.

34. The dental restorative composition of claim 33 used as a filling material or as a cement.

### Patentansprüche

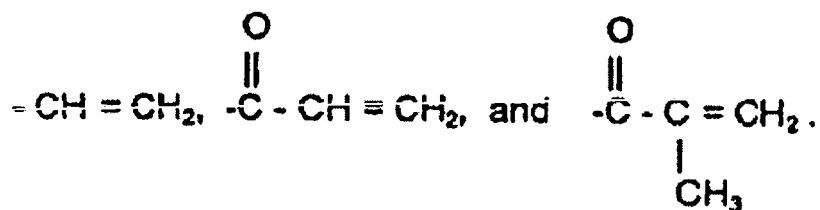
1. Zahnrestaurationszusammensetzung umfassend

(a) ein erstes alkoxyliertes und trifunktionelles Monomer der allgemeinen Formel



wobei G eine Alkylenoxideinheit ist und  $6 \leq x + y + z \leq 30$  ist und  $R_3$  ethylenisch ungesättigte Gruppen sind,  
 (b) ein zweites Monomer, das mit dem ersten Monomer copolymerisieren kann und mindestens eine ethylenisch ungesättigte Gruppe umfasst, wobei das zweite Monomer unter mindestens einem von Hydroxyethyl(meth)acrylat, Hydroxypropyl(meth)acrylat, Hydroxybutyl(meth)acrylat, Glycerindi(meth)acrylat, Glycerinmono(meth)acrylat, Methyl(meth)acrylat, Ethyl(meth)acrylat, Propyl(meth)acrylat, Butyl(meth)acrylat, Hexyl(meth)acrylat, Octyl(meth)acrylat, Lauryl(meth)acrylat, Decyl(meth)acrylat, Tridecyl(meth)acrylat; 2-Ethoxyethyl(meth)acrylat, 2-Ethoxy-2-ethoxyethyl(meth)acrylat, Ethylenglykoldi(meth)acrylat, Diethylenglykoldi(meth)acrylat, Triethylenglykoldi(meth)acrylat, Tetraethylenglykoldi(meth)acrylat, Polyethylenglykolmono(meth)acrylat, Polyethylenglykoldi(meth)acrylat, Polypropylenglykolmono(meth)acrylat, Polypropylenglykoldi(meth)acrylat, Polytetramethylenglykolmono(meth)acrylat, Polytetramethylenglykoldi(meth)acrylat, Hexandioldi(meth)acrylat, Trimethylolpropantri(meth)acrylat, UDMA, Bis-GMA, EBPADMA-n, Tetrahydrofurfuryl (meth)acrylat oder TEGDMA oder einer Mischung derselben ausgewählt wird und  
 (c) einen Polymerisationsinitiator.

2. Zahnrestaurationszusammensetzung nach Anspruch 1, wobei  $R_1$ ,  $R_2$  und  $R_3$  aus der Gruppe ausgewählt sind bestehend aus



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3. Zahnrestaurationszusammensetzung nach einem der vorhergehenden Ansprüche, wobei  $x + y + z$  im Bereich von 3 bis 15 liegt.
  4. Zahnrestaurationszusammensetzung nach Anspruch 1, wobei das erste Monomer eine Kombination von mindestens zwei verschiedenen trifunktionellen Monomeren umfasst und der Mittelwert von  $(x + y + z) \geq 3$  und  $\leq 30$  ist.
  5. Zahnrestaurationszusammensetzung nach Anspruch 1, wobei das erste Monomer eine Kombination von mindestens zwei verschiedenen trifunktionellen Monomeren umfasst und der Mittelwert von  $(x + y + z)$  im Bereich von 3 bis 15 liegt.
  6. Zahnrestaurationszusammensetzung nach einem der vorhergehenden Ansprüche, wobei G  $-\text{OC}_n\text{H}_{2n}-$  ist und n im Bereich zwischen 1 und 12 liegt.
  7. Zahnrestaurationszusammensetzung nach einem der vorhergehenden Ansprüche, wobei G eine lineare oder verzweigte Alkylenoxideinheit ist.
  8. Zahnrestaurationszusammensetzung nach einem der vorhergehenden Ansprüche, des Weiteren einen feinverteilten Füllstoff umfassend.
  9. Zahnrestaurationszusammensetzung nach Anspruch 8, wobei der Füllstoff aus der Gruppe ausgewählt ist bestehend aus anorganischem Metall, Salz, Oxid, Silicat, Aluminosilicat, Aluminoborsilicat, Fluoraluminosilicat, kolloidalem Siliciumdioxid, ausgefälltem Siliciumdioxid, polymerem Füllstoff, polymerisiertem Verbundfüllstoff mit anorganischen Teilchen und Kombinationen derselben.
  10. Zahnrestaurationszusammensetzung nach Anspruch 8, wobei der Füllstoff aus der Gruppe ausgewählt ist bestehend aus Bariumaluminosilicat, Bariumaluminoborsilicat, Strontiumaluminosilicat, Zinkaluminosilicat, Bariumaluminofluorsilicat, Strontiumaluminofluorsilicat, pyrogenem Siliciumdioxid und Kombinationen derselben.
  11. Zahnrestaurationszusammensetzung nach einem der Ansprüche 8 bis 10, wobei der Füllstoff eine mittlere Teilchengröße von weniger als  $15 \mu\text{m}$  aufweist.
  12. Zahnrestaurationszusammensetzung nach einem der Ansprüche 8 bis 10, wobei der Füllstoff eine mittlere Teilchengröße von weniger als  $5 \mu\text{m}$  aufweist.
  13. Zahnrestaurationszusammensetzung nach einem der Ansprüche 8 bis 10, wobei der Füllstoff eine mittlere Teilchengröße von weniger als  $2 \mu\text{m}$  aufweist.
  14. Zahnrestaurationszusammensetzung nach einem der Ansprüche 8 bis 13, wobei der Füllstoff einen Nanoteilchenfüllstoff umfasst.
  15. Zahnrestaurationszusammensetzung nach einem der Ansprüche 8 bis 14, wobei der Füllstoff eine mittlere Teilchengröße im Bereich von 5 nm bis 200 nm aufweist.
  16. Zahnrestaurationszusammensetzung nach einem der Ansprüche 8 bis 15, wobei der Füllstoff mit einem Haftvermittler oberflächenbehandelt oder oberflächenbeschichtet ist.
  17. Zahnrestaurationszusammensetzung nach Anspruch 16, wobei der Haftvermittler  $\gamma$ -Methacryloyloxypropyltrimethoxysilan ist.

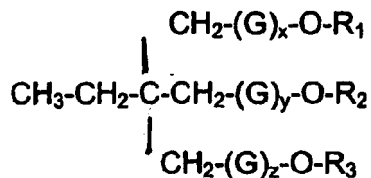
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18. Zahnrestaurationszusammensetzung nach einem der vorhergehenden Ansprüche, wobei der Polymerisationsinitiator aus der Gruppe ausgewählt ist bestehend aus einem Photoinitiatorsystem, einem Redoxinitiatorsystem und Kombinationen derselben.
- 5 19. Zahnrestaurationszusammensetzung nach einem der vorhergehenden Ansprüche, wobei die Zusammensetzung eine lichtaushärtende Einkomponentenzusammensetzung ist, die ein Photoinitiatorsystem aufweist.
20. Zahnrestaurationszusammensetzung nach einem der Ansprüche 1 bis 18, wobei die Zusammensetzung eine selbstaushärtende Zweikomponentenzusammensetzung ist, die ein Redoxinitiatorsystem aufweist.
- 10 21. Zahnrestaurationszusammensetzung nach einem der Ansprüche 1 bis 18, wobei die Zusammensetzung eine Dualaushärtungs-Zweikomponentenzusammensetzung ist, die ein kombiniertes Photoinitiator- und Redoxinitiatorsystem aufweist.
- 15 22. Zahnrestaurationszusammensetzung nach einem der Ansprüche 18, 19 oder 21, wobei das Photoinitiatorsystem einen Photosensibilisator und einen Aktivator umfasst.
23. Zahnrestaurationszusammensetzung nach Anspruch 22, wobei der Photosensibilisator Kampferchinon ist.
- 20 24. Zahnrestaurationszusammensetzung nach entweder Anspruch 22 oder Anspruch 23, wobei der Aktivator ein tertiäres Amin ist.
- 25 25. Zahnrestaurationszusammensetzung nach einem der Ansprüche 18, 20 oder 21, wobei das Redoxinitiatorsystem ein Oxidationsmittel und ein Reduktionsmittel umfasst.
26. Zahnrestaurationszusammensetzung nach Anspruch 25, wobei das Oxidationsmittel ein Peroxid ist.
27. Zahnrestaurationszusammensetzung nach entweder Anspruch 25 oder Anspruch 26, wobei das Reduktionsmittel aus der Gruppe ausgewählt ist bestehend aus einem tertiären Amin, einer Sulfinsäure, einem Alkalimetallsulfinat und Kombinationen derselben.
- 30 28. Zahnrestaurationszusammensetzung nach einem der vorhergehenden Ansprüche, des Weiteren ein Lösungsmittel umfassend ausgewählt aus der Gruppe bestehend aus Wasser, Aceton, Methanol, Ethanol, Isopropanol und Kombinationen derselben.
- 35 29. Zahnrestaurationszusammensetzung nach einem der vorhergehenden Ansprüche, des Weiteren einen Stabilisator umfassend.
- 40 30. Zahnrestaurationszusammensetzung nach einem der vorhergehenden Ansprüche, des Weiteren einen UV-Stabilisator umfassend.
- 45 31. Zahnrestaurationszusammensetzung nach einem der vorhergehenden Ansprüche, wobei die Zusammensetzung aus der Gruppe ausgewählt ist bestehend aus Harzverbundstoff, einem Harzionomer und einem harzmodifizierten Glas-Ionomer.
- 50 32. Zahnrestaurationszusammensetzung nach einem der vorhergehenden Ansprüche, die als Füllmaterial, Zement, Verkleidung, Base, Klebstoff oder Kombination derselben verwendet wird.
33. Zahnrestaurationszusammensetzung nach einem der Ansprüche 8 bis 31, wie von Anspruch 1 abhängig, wobei G aus der Gruppe ausgewählt ist bestehend aus Ethylenoxid, n-Propylenoxid, Isopropylenoxid, n-Butylenoxid und Kombinationen derselben,  $3 \leq x + y + z < 20$  ist und  $R_1$ ,  $R_2$  und  $R_3$  unabhängig aus der Gruppe ausgewählt sind bestehend aus Acrylat und Methacrylat.
- 55 34. Zahnrestaurationszusammensetzung nach Anspruch 33, die als Füllmaterial oder Zement verwendet wird.

## Revendications

1. Une composition pour restauration dentaire comprenant

(a) un premier monomère alkoxyaté et trifonctionnel de la formule générale

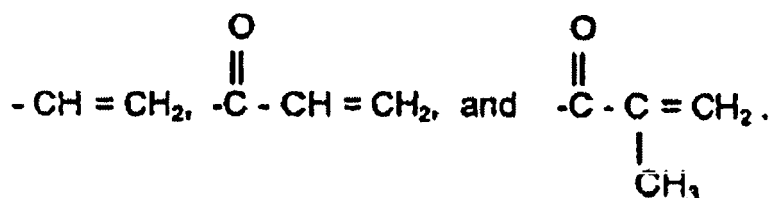


selon laquelle G est une unité d'oxyde d'alkylène, et  $6 \leq x + y + z \leq 30$  et  $R_3$  sont des groupes éthyléniquement insaturés,

(b) un deuxième monomère qui peut se co-polymériser avec le premier monomère comprenant au moins un groupe éthyléniquement insaturé, le deuxième monomère étant sélectionné dans au moins un de : (méth)acrylate d'hydroxyéthyle, (méth)acrylate d'hydroxypropyle, (méth)acrylate d'hydroxybutyle, di(méth)acrylate de glycérol, mono(méth)acrylate de glycérol, (méth)acrylate de méthyle, (méth)acrylate d'éthyle, (méth)acrylate de propyle, (méth)acrylate de butyle, (méth)acrylate d'hexyle, (méth)acrylate d'octyle, (méth)acrylate de lauryle, (méth)acrylate de décyle, (méth)acrylate de tridécyle, (méth)acrylate de 2-éthoxyéthyle, (méth)acrylate de 2-éthoxy-2-éthoxyéthyle, di(méth)acrylate d'éthylène glycol, di(méth)acrylate de diéthylène glycol, di(méth)acrylate de triéthylène glycol, di(méth)acrylate de tétraéthylène glycol, mono-(méth)acrylate de polyéthylène glycol, di-(méth)acrylate de polyéthylène glycol, mono-(méth)acrylate de polypropylèneglycol, di-(méth)acrylate de polypropylène glycol, mono-(méth)acrylate de polytétraméthylène glycol, di(méth)acrylate de polytétraméthylène glycol, di(méth)acrylate d'hexanédiol, tri(méth)acrylate de triméthylolpropane, UDMA, Bis-GMA, EB-PADMA-n, (méth)acrylate de tétrahydrofurfuryle ou TEGDMA ou un mélange de ceux-ci, et

(c) un amorceur de polymérisation.

2. Composition pour restauration dentaire selon la revendication 1 dans laquelle  $R_1$ ,  $R_2$  et  $R_3$  sont sélectionnés dans le groupe constitué de



3. Composition pour restauration dentaire selon l'une quelconque revendication précédente dans laquelle  $x + y + z$  se situe dans la plage de 3 à 15.
4. Composition pour restauration dentaire selon la revendication 1 dans laquelle le premier monomère comprend une combinaison d'au moins deux monomères trifonctionnels différents et la moyenne  $(x+y+z)$  est  $\geq 3$  et  $\leq 30$ .
5. Composition pour restauration dentaire selon la revendication 1 dans laquelle le premier monomère comprend une combinaison d'au moins deux monomères trifonctionnels différents et la moyenne  $(x+y+z)$  est comprise dans la plage de 3 à 15.
6. Composition pour restauration dentaire selon l'une quelconque revendication précédente dans laquelle G est  $-\text{OC}_n\text{H}_{2n}-$  et n est compris dans la plage de 1 à 12.
7. Composition pour restauration dentaire selon l'une quelconque revendication précédente dans laquelle G est une

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unité d'oxyde d'alkylène linéaire ou à radical branché.

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8. Composition pour restauration dentaire selon l'une quelconque revendication précédente contenant en outre un matériau obturateur finement divisé.
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9. Composition pour restauration dentaire selon la revendication 8 dans laquelle le matériau obturateur est choisi parmi le groupe constitué de métal inorganique, sel, oxyde, silicate, aluminosilicate, aluminoborosilicate, fluoroaluminosilicate, silice colloïdal, silice précipité, matériau obturateur polymérique, matériau obturateur composite polymérisé avec particules inorganiques et combinaisons de ceux-ci.
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10. Composition pour restauration dentaire selon la revendication 8 dans laquelle le matériau obturateur est choisi parmi le groupe constitué d'aluminosilicate de baryum, aluminoborosilicate de baryum, aluminosilicate de strontium, aluminosilicate de zinc, aluminofluorosilicate de baryum, aluminofluorosilicate de strontium, oxyde de silicium fumigé et combinaisons de ceux-ci.
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11. Composition pour restauration dentaire de l'une quelconque des revendications 8 à 10 dans laquelle le matériau obturateur a une taille particulière moyenne de moins de 15  $\mu\text{m}$ .
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12. Composition pour restauration dentaire de l'une quelconque des revendications 8 à 10 dans laquelle le matériau obturateur a une taille particulière moyenne de moins de 5  $\mu\text{m}$ .
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13. Composition pour restauration dentaire de l'une quelconque des revendications 8 à 10 dans laquelle le matériau obturateur a une taille particulière moyenne de moins de 2  $\mu\text{m}$ .
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14. Composition pour restauration dentaire de l'une quelconque des revendications 8 à 13 dans laquelle le matériau obturateur comporte un matériau obturateur nano-particulaire.
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15. Composition pour restauration dentaire de l'une quelconque des revendications 8 à 14 dans laquelle le matériau obturateur a une taille particulière moyenne comprise dans la plage de 5 nm à 200 nm.
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16. Composition pour restauration dentaire de l'une quelconque des revendications 8 à 15 dans laquelle le matériau obturateur est traité en surface ou est revêtu en surface d'un agent de couplage.
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17. Composition pour restauration dentaire selon la revendication 16 dans laquelle l'agent de couplage est du  $\gamma$ -méthacryloyloxypropyltriméthoxysilane.
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18. Composition pour restauration dentaire selon l'une quelconque revendication précédente dans laquelle l'amorceur de la polymérisation est sélectionné dans le groupe constitué d'un système photoamorceur, d'un système amorceur d'oxydo-réduction et de combinaisons de ceux-ci.
19. Composition pour restauration dentaire de l'une quelconque revendication précédente dans laquelle la composition est une partie de composition photopolymérisable possédant un système photoamorceur.
20. Composition pour restauration dentaire de l'une quelconque des revendications 1 à 18 dans laquelle la composition est deux parties de composition à auto-durcissement possédant un système amorceur d'oxydo-réduction.
21. Composition pour restauration dentaire de l'une quelconque des revendications 1 à 18 dans laquelle la composition est deux parties de composition à double durcissement possédant un système photoamorceur et amorceur d'oxydo-réduction combiné.
22. Composition pour restauration dentaire de l'une quelconque des revendications 18, 19 ou 21 dans laquelle le système photoamorceur comporte un photosensibilisateur et un activateur.
23. Composition pour restauration dentaire selon la revendication 22 dans laquelle le photosensibilisateur est du quinone de camphre.
24. Composition pour restauration dentaire de l'une quelconque des revendications 22 ou 23 dans laquelle l'activateur est une amine tertiaire.

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25. Composition pour restauration dentaire de l'une quelconque des revendications 18, 20 ou 21 dans laquelle le système amorceur d'oxydo-réduction comporte un oxydant et un réducteur.
- 5 26. Composition pour restauration dentaire selon la revendication 25 dans laquelle l'oxydant est un peroxyde.
27. Composition pour restauration dentaire de l'une quelconque des revendications 25 ou 26 dans laquelle le réducteur est sélectionné dans le groupe constitué d'une amine tertiaire, d'un acide sulfinique, d'un sulfinate de métal alcalin et de combinaisons de ceux-ci.
- 10 28. Composition pour restauration dentaire selon l'une quelconque revendication précédente comprenant en outre un solvant sélectionné dans le groupe constitué d'eau, acétone, méthanol, éthanol, isopropanol et combinaisons de ceux-ci.
- 15 29. Composition pour restauration dentaire selon l'une quelconque revendication précédente comprenant en outre un stabilisant.
30. Composition pour restauration dentaire selon l'une quelconque revendication précédente comprenant en outre un stabilisant anti-UV.
- 20 31. Composition pour restauration dentaire selon l'une quelconque revendication précédente dans laquelle le matériau obturateur est sélectionné dans le groupe constitué de résine composite, résine ionomère et ionomère de verre modifié par apport de résine.
- 25 32. Composition pour restauration dentaire selon l'une quelconque revendication précédente utilisée comme matériau obturateur, ciment, fond, base, adhésif ou une combinaison de ceux-ci.
- 30 33. Composition pour restauration dentaire de l'une des revendications 8 à 31 en tant que dépendantes selon la revendication 1 selon laquelle G est sélectionné dans le groupe constitué d'oxyde d'éthylène, oxyde de n-propylène, oxyde d'isopropylène, oxyde de n-butylène et combinaisons de ceux-ci,  $3 \leq x + y + z \leq 20$  et  $R_1$ ,  $R_2$  et  $R_3$  étant sélectionnés indépendamment dans le groupe constitué d'acrylate et de méthacrylate.
- 35 34. Composition pour restauration dentaire selon la revendication 33 utilisée comme matériau obturateur ou comme ciment.

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**REFERENCES CITED IN THE DESCRIPTION**

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