(12) UK Patent Application (19) GB (11) 2 173 206 A

(43) Application published 8 Oct 1986

(21) Application No 8607794

(22) Date of filing 27 Mar 1986

(30) Priority data

(31) 60/068533 (32) 2 Apr 1985 (33) JP

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(51) INT CL[4]
A61K 6/04

(52) Domestic classification (Edition H):
C3V BF
C3K 101 MA
C3W 100 225 301
U1S 1028 3035 3079 C3K C3V

(56) Documents cited
GB 1425291
GB 1122439
EP A 0046354
US 3513123

(58) Field of search
C3V
C3K

(54) Dental composite resin composition

(57) A dental composite resin composition comprises:
a polymerizable monomer, an inorganic and/or organic filler, a gold powder and/or a gold-color alloy powder, and a polymerization catalyst. The dental composite resin composition of the present invention is useful as a filling material for repairing a tooth cavity, has a gold-color luster and exhibits excellent abrasion resistance as well as excellent X-ray contrast.

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SPECIFICATION

Dental composite resin composition

The present invention relates to a dental composite resin composition useful as a filling material for repairing a tooth cavity.

As filling materials used in dentistry, dental amalgams which are prepared by mixing a dental amalgan alloy powder and mercury have hitherto been mainly employed. However, since such dental amalgams use mercury which is harmful to human bodies and is an environmental pollutant, in recent years dental composite resin compositions have become widely used as a replacement for dental amalgams in view of safety.

Such a dental composite resin composition is generally composed of a polymerizable monomer, an inorganic filler and/or an organic filler, a polymerization catalyst, a pigment, and a stabilizer, and is usually in the form of two types of pastes in which one paste is incorporated with peroxide (as one catalyst component) and the other paste is incorporated with an amine or sulfinic acid (as the other catalyst component). These two pastes are mixed at the time of use and then polymerized.

These dental composite resin compositions are generally classified, depending upon the type of the filler used, into conventional type composite resins having an irregular particle sized filler of about 1 - 50 μm, such as silica, quartz, barium glass, lithium aluminium silicate, and ceramics, and MFR (microparticle filled resin) type composite resins having superfine sized silica filler of 0.005 - 0.04 μm.

However, the above-described dental composite resin composition has a poor abrasion resistance in that its cured material is readily abraded by mastication of foods as compared with the dental amalgam. In particular, the cured conventional type composite resin composition is such that after abrasion in an oral cavity, its surface becomes rough. In order to solve the problem of the rough surface, MFR has been developed, but its abrasion resistance is rather reduced. Further, while the X-ray contrast is a very useful property in diagnosis by a dentist, when a compound such as barium, lead, tungsten, or zirconium is added as a X-ray contrast medium to the dental composite resin composition, the mechanical properties are decreased and the color tone is deteriorated, and hence it is difficult to impart a satisfactory X-ray contrast.

In order to overcome the drawbacks of the above-described dental composite resin composition, the present inventors have made extensive investigations and found that it is effective to add a gold powder and/or a gold-color alloy powder to the dental composite resin composition.

The present invention provides a dental composite resin composition comprising as main components a polymerizable monomer, an inorganic filler and/or an organic filler, a gold powder and/or a gold-color alloy powder, and a polymerization catalyst.

The invention thus provides a dental composite resin composition which contains a gold powder and/or a gold-color alloy powder. The dental composite resin composition of the invention not only has excellent aesthetic properties for dental use but is also quite effective as a means for improving the X-ray contrast because of containing the gold powder and/or gold-color alloy powder. Further, it can improve the surface smoothness and the surface hardness without reducing the abrasion resistance of the cured dental composite resin. It is considered that this is caused by the metal powder present in the surface layer work hardening by polishing or mastication over a long period of time to thereby strengthen the matrix.

Examples of the gold powder or gold-color alloy powder which can be used in the present invention include gold powder, gold base alloy powder, Cu-Zn base alloy powder, Cu-Al base alloy powder, In-Pd base alloy powder, Zn-Pd base alloy powder, TiN powder, etc. Among them, the gold powders, and gold base alloy powders, are preferred because they are free from tarnish in the oral cavity and are excellent in X-ray contrast.

A suitable amount of the gold powder and/or gold-color alloy powder which is incorporated into the dental composite resin composition is in the range of from 1 to 60 % by weight. If the amount is too large, the physical properties tend to be decreased, whereas if it is too small, the desired effects cannot be exhibited satisfactorily.

A suitable particle size of the gold powder or gold-color alloy powder which is used is 50μm or less and preferably 20 μm or less. If the particle size is too large, not only is the workability deteriorated but also the surface of the cured material tends to become rough.

With respect to the shape of particles of the gold powder or gold-color alloy powder, there is no particular restriction, but thin foil-like or flake-like ones are preferred for the appearance of metallic color.

Though the gold powder or gold-color alloy powder can be incorporated as it stands, it is preferred to effect surface treatment with a silane coupling agent. Examples of the silane coupling agent which can be used include vinyl trichlorosilane, vinyl triethoxysilane, vinyl trimethoxysilane, vinyl tris (β-methoxyethoxy) silane, and γ-methacryloxypropyl trimethoxysilane.

The polymerizable monomer which is used in the present invention may be either a monofunctional monomer or a polyfunctional monomer.

Examples of the monofunctional monomer include methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, acryl acrylate, acryl methacrylate, hydroxyethyl acrylate, hydroxyethyl methacrylate, methoxyethyl acrylate, and methoxyethyl methacrylate. Examples of the polyfunctional monomer include bifunctional aliphatic acrylates, bifunctional aliphatic methacrylates,

bifunctional aromatic acrylates, bifunctional aromatic methacrylates, trifunctional aliphatic acrylates, trifunctional aliphatic methacrylates, tetrafunctional acrylates, and tetrafunctional methacrylates, such as triethylene glycol diacrylate, triethylne glycol dimethacrylate, 2,2-bis(4-methacryloxyphenyl)propane, 2,2-bis(4-methacryloxy-ethoxyphenyl)propane, 2,2-bis(4-methacryloxypolyethoxyphenyl)-propane, 2,2-bis[4-(methacryloxy-2-hydroxypropoxy)-phenyl]-propane, di(methacryloxyethyl) trimethylhexamethylene di-urethane, tetramethylolmethane tetraacrylate, and tetramethylolmethane tetramethacrylate. These polymerizable monomers can be used alone or in admixture of two or more thereof.

As the filter which is used in the present invention, inorganic fillers such as silica powder, quartz, glass beads, aluminium oxide, and ceramics are usually used. A suitable particle size of the inorganic filler is generally 50μm or less, but those fine particles having a particle diameter of 10μm or less are preferred from the standpoint of smoothness of the surface. These particles can be, as a matter of course, used in combination. Further, though the inorganic filler can be added alone, it is preferred to previously subject to surface treatment with a silane coupling agent. Examples of the silane coupling agent which can be used include vinyl trichlorosilane, vinyl triethoxysilane, vinyl trimethoxysilane, vinyl tris(β-methoxyethoxy)silane, and α-methacryloxypropyl trimethoxysilane. Moreover, an organic filler prepared by mixing superfinely divided silica and the polymerizable monomer, polymerizing and curing it, and then pulverizing the polymer can also be used as the filler.

A suitable amount of the filler which is incorporated into the dental composite resin composition is usually in the range of about 20~80 % by weight.

As the polymerization catalyst which is used in the present invention, known catalysts such as, for example, a so-called redox catalyst, e.g., a combination of amines and peroxides or a combination of sulfinic acids and peroxides, can be used. Examples of the peroxide include diacyl peroxide group such as benzoyl peroxide, p-chlorobenzoyl peroxide, 2,4-dichlorobenzoyl peroxide, acetyl peroxide, and lauroyl peroxide; hydroperoxide group such as t-butyl hydroperoxide, cumene hydroperoxide, and 2,5-dimethylhexane 2,5-dihydroperoxide; ketone peroxide group such as methyl ethyl ketone peroxide; and peroxycarbonate group such as t-butyl peroxybenzoate.

Examples of the amine which is combined with the above-described peroxide include N,N-bis-(2-hydroxyethyl)-4-methylaniline, N,N-bis-(2-hydroxyethyl)-3,4-dimethylaniline, N,N-bis-(2-hydroxyethyl)-3,5-dimethylaniline, N-methyl-N-(2-hydroxyethyl)-4-methylaniline, 4-methylaniline, N,N-dimethyl-p-toluidine, N,N-dimethylaniline, and triethanolamine. Examples of the sulfinic acid which is combined with the peroxide include p-toluenesulfinic acid, benzene-sulfinic acid, and salts thereof. Further, examples of other material which is combined with the peroxide include cobalt naphthenate, cobalt octanate, trimethyl barbituric acid, and a trialkyl boron. In using the polymerization catalyst, a mixture of the above-described polymerizable monomer and filler is divided into two parts, the amine or sulfinic acid is incorporated into one part whereas the peroxide is incorporated into the other part, and the both parts are mixed at the time of use.

If desired, known pigments, stabilizers and the like can be added to the dental composite resin composition according to the present invention. Examples of stabilizer include hydroquinone, hydroquinone monomethyl ether, t-butyl paracresol and hydroxy methoxybenzophenone.

A filling material using the dental composite resin composition comprising the above-described components according to the present invention is markedly easy in workability as compared with an inlay by casting of a metal, is inexpensive in cost, and is light in weight. Further, it exhibits a gold color in external appearance like an inlay by a gold alloy and is free from tarnish even after use in an oral cavity over a long period of time, and hence it gives to patients confidence as in an inlay by gold alloy. Still further, the dental composite resin composition of the present invention has a smooth surface and an excellent surface hardness comparable to the conventional ones and provides useful X-ray contrast in diagnosis by a dentist, and hence it possesses suitable properties as a dental composite resin composition.

The present invention will be further described with reference to the following examples.

Examples

Pastes A to P each having the following composition were prepared.

Paste A

2,2-Bis[4-(3-methacryloxy-2-hydroxypropyl)-phenyl]-propane: 15.5 parts by weight
Triethylene glycol dimethacrylate: 15.5 parts by weight
Quartz treated with γ-methacryloxypropyl trimethoxysilane (50 μm or less): 67.5 parts by weight
Benzoyl peroxide: 1.5 parts by weight
Hydroquinone monomethyl ether: 0.01 part by weight

Paste A'

2,2-Bis[4-(3-methacryloxy-2-hydroxypropyl)-phenyl]-propane: 15.5 parts by weight
Triethylene glycol dimethacrylate: 15.5 parts by weight
Quartz treated with γ-methacryloxypropyl trimethoxysilane (50 μm or less): 67.0 parts by weight
N,N-Dimethyl-p-toluidine: 2.0 parts by weight
Hydroquinone monomethyl ether: 0.01 part by weight

Paste B

The above paste A: 50 parts by weight. A gold powder (20 μm or less): 50 parts by weight.

Paste B'

The above paste A': 50 parts by weight. A gold powder (20 μm or less): 50 parts by weight.

Paste C

The above paste A: 80 parts by weight. A gold powder (20 μm or less): 20 parts by weight.

Paste C'

The above paste A': 80 parts by weight. A gold powder (20 μm or less): 20 parts by weight.

Paste D

The above paste A: 85 parts by weight. A powder (20μm or less) of a gold base allow (75 wt% Au-12.5 wt% Ag-12.5 wt% Cu) treated with γ-methacryloxypropyl trimethoxy-silane: 15 parts by weight.

Paste D'

The above paste A': 85 parts by weight. A powder (20 μm or less) of a gold base alloy (75 wt% Au-12.5 wt% Ag-12.5 wt% Cu) treated with γ-methacryloxypropyl trimethoxy-silane: 15 parts by weight.

Paste E

The above paste A: 55 parts by weight. A powder (44 μm or less) of a gold base alloy (60 wt% Au-20 wt% Cu-18 wt% Ag-2 wt% Zn) treated with vinyl trimethoxysilane: 45 parts by weight.

Paste E'

The above paste A': 55 parts by weight. A powder (44 μm or less) of a gold base alloy (60 wt% Au-20 wt% Cu-18 wt% Ag-2 wt% Zn) treated with vinyl trimethoxysilane: 45 parts by weight.

Paste F

The above paste A: 65 parts by weight. A gold powder (50 μm or less) treated with γ-methacryloxypropyl trimethoxysilane: 35 parts by weight.

Paste F'

The above paste A': 65 parts by weight. A gold powder (50 μm or less) treated with γ-methacryloxypropyl trimethoxysilane: 35 parts by weight.

Paste G

Di(methacryloxyethyl) trimethylhexamethylene diurethane: 24.0 parts by weight
Triethylene glycol dimethacrylate: 16.0 parts by weight
Organic filler (50 μm or less) which was prepared by block polymerizing a composition of 50 parts by weight of finely divided silica (particle size: 50 m μm or less), 30 parts by weight of di(methacryloxyethyl) trimethylhexamethylene diurethane, 20 parts by weight of triethylene glycol dimethacrylate and 1 part by weight of benzoyl peroxide and pulverizing the polymer by means of a mill to 50 μm or less: 58.5 parts by weight
Benzoyl peroxide: 1.5 parts by weight
Hydroquinone monomethyl ether: 0.01 part by weight

Paste G'

Di(methacryloxyethyl) trimethylhexamethylene diurethane: 24.0 parts by weight
Triethylene glycol dimethacrylate: 16.0 parts by weight
Organic filler (50 μm or less) which was prepared by block polymerizing a composition of 50 parts by weight of finely divided silica (particle size: 50 m μm of less), 30 parts by weight of di(methacryloxyethyl) trimethylhexamethylene diurethane, 20 parts by weight of triethylene glycol dimethacrylate and 1 part by weight of benzoyl peroxide and pulverizing the polymer by means of a mill to 50 μm or less: 58.0 parts by weight
N,N-Dimethyl-p-toluidine: 2.0 parts by weight
Hydroquinone monomethyl ether: 0.01 part by weight

Paste H

The above paste G: 45 parts by weight. A gold powder (20 μm or less) treated with γ-methacryloxypropyl trimethoxysilane: 55 parts by weight.

Paste H'

The above paste G':45 parts by weight. A gold powder (20 μm or less) treated with γ-methacryloxypropyl trimethoxysilane: 55 parts by weight.

Paste I
The above paste G: 95 parts by weight. A powder (20 μm or less) of a In-Pd alloy (50 wt% In-50 wt% Pd): 5 parts by weight.

Paste I'
The above paste G': 95 parts by weight. A powder (20 μm or less) of a In-Pd alloy (50 wt% In-50 wt% Pd): 5 parts by weight.

Paste J
The above paste G: 70 parts by weight. A gold powder (20 μm or less) treated with γ-methacryloxypropyl trimethoxysilane: 30 parts by weight.

Paste J'
The above paste G': 70 parts by weight. A gold powder (20 μm or less) treated with γ-methacryloxypropyl trimethoxysilane: 30 parts by weight.

Paste K
The above paste G: 90 parts by weight. A gold powder (20 μm or less) treated with vinyl trimethoxysilane: 10 parts by weight.

Paste K'
The above paste G': 90 parts by weight. A gold powder (20 μm or less) treated with vinyl trimethoxysilane: 10 parts by weight.

Paste L
Di(methacryloxyethyl) trimethylhexamethylene diurethane: 18.0 parts by weight
Triethylene glycol dimethacrylate: 12.0 parts by weight
Organic filler (50 μm or less) which was prepared by block polymerizing a composition of 50 parts by weight of finely divided silica (particle size : 50 m μm or less), 30 parts by weight of di(methacryloxyethyl) trimethylhexamethylene diurethane, 20 parts by weight of triethylene glycol dimethacrylate and 1 part by weight of benzoyl peroxide and pulverizing the polymer by means of a mill to 50 μm or less: 49. parts by weight
Glass beads (50 μm or less) treated with vinyl trimethoxysilane: 19.5 parts by weight
Benzoyl peroxide: 1.5 parts by weight
Hydroquinone monomethyl ether: 0.01 part by weight

Paste L'
Di(methacryloxyethyl) trimethylhexamethylene diurethane: 18.0 parts by weight
Triethylene glycol dimethacrylate: 12.0 parts by weight
Organic filler (50 μm or less) which was prepared by block polymerizing a composition of 50 parts by weight of finely divided silica (particle size : 50 m μm or less), 30 parts by weight of di(methacryloxyethyl) trimethylhexamethylene diurethane, 20 parts by weight of triethylene glycol dimethacrylate and 1 part by weight of benzoyl peroxide and pulverizing the polymer by means of a mill to 50 μm or less: 48.5 parts by weight
Glass beads (50 μm or less) treated with vinyl trimethoxysilane: 19.5 parts by weight
N,N-dimethyl-p-toludine: 2.0 parts by weight
Hydroquinone monomethyl ether: 0.01 part by weight

Paste M
The above paste L: 60 parts by weight. A gold powder (20 μm or less) treated with vinyl trimethoxysilane: 40 parts by weight.

Paste M'
The above paste L': 60 parts by weight. A gold powder (20 μm or less) treated with vinyl trimethoxysilane: 40 parts by weight.

Paste N
The above paste L: 60 parts by weight. A powder (44 μm or less) of a gold base alloy (90 wt % Au-10 wt% Ag): 40 parts by weight.

Paste N'
The above paste L': 60 parts by weight. A powder (44 μm or less) of a gold base alloy (90 wt% Au-10 wt% Ag) 40 parts by weight.

Paste O

The above paste L: 90 parts by weight. A gold powder (20 μm or less) treated with vinyl trimethoxysilane: 10 parts by weight.

Paste O'

The above paste L' : 90 parts by weight. A gold powder (20 μm or less) treated with vinyl trimethoxysilane: 10 parts by weight.

Paste P

The above paste L: 99.5 parts by weight. A powder (20 μm or less) of a TiN treated with vinyl trimethoxysilane: 0.5 parts by weight.

Each of the above-described pastes was prepared by mixing and dissolving the polymerizable monomer, dissolving the polymerization catalyst for the polymerizable monomer as well as the stabilizer, and then adding thereto the filler and the gold powder and/or gold-color alloy powder, followed by degassing and kneading. Thereafter, based on the combination of Examples 1 to 20 and Comparative Examples 1 to 4 shown in the table below, the same amount of each of the pastes was taken and mixed. As a result, all of the pastes were cured within 8 minutes.

Further, in order to evaluate the properties of the cured material, a disc-like cured material having a size of 10 mmø × 5 mm was prepared by using the same amount of each of the pastes based on the combination of each of Examples 1 to 20 and Comparative Examples 1 to 4, and the measurement of surface hardness, the measurement of wear depth by the abrasion test, and the X-ray contrast were evaluated.

In the above evaluation, the measurement of surface hardness was carried out by measuring the Knoop hardness at a load of 200 g for 30 seconds.

The measurement of wear depth by the abrasion test was carried out by the toothbrush test by 50,000 times using a commercially available toothbrush and tooth paste.

The X-ray contrast was carried out by placing each cured material on an X-ray film, irradiating it with X-rays, and then developing the X-ray film.

The results obtained are shown in the table below.

Example and Comparative Example No. *	Hardness of Surface (Hk)	Wear Depth by Abrasion Test (cm)	X-Ray Contrast
Ex. 1	82	1.55×10^{-5}	Good
" 2	77	1.66×10^{-5}	"
" 3	75	1.77×10^{-5}	"
" 4	76	1.73×10^{-5}	"
" 5	82	1.56×10^{-5}	"
" 6	80	1.60×10^{-5}	"
" 7	73	1.79×10^{-5}	"
" 8	77	1.67×10^{-5}	"
" 9	52	3.11×10^{-5}	"
" 10	41	3.57×10^{-5}	"
" 11	48	3.29×10^{-5}	"
" 12	43	3.50×10^{-5}	"
" 13	41	3.55×10^{-5}	"
" 14	50	3.31×10^{-5}	"
" 15	77	2.50×10^{-5}	"
" 16	78	2.52×10^{-5}	"
" 17	78	2.50×10^{-5}	"
" 18	66	2.92×10^{-5}	"
" 19	70	2.76×10^{-5}	"
" 20	63	3.02×10^{-5}	"
Com. Ex. 1	68	1.87×10^{-5}	Nil
" 2	31	4.08×10^{-5}	"
" 3	57	3.71×10^{-5}	"
" 4	57	3.69×10^{-5}	Weak

Ex. 1: cured material of paste B and paste B'
Ex. 2: cured material of paste C and paste C'
Ex. 3: cured material of paste A and paste C'

Ex. 4: cured material of paste D and paste D'
Ex. 5: cured material of paste E and paste E'
Ex. 6: cured material of paste F and paste F'
Ex. 7: cured material of paste D and paste A'
Ex. 8: cured material of paste D and paste C'
Ex. 9: cured material of paste H and paste H'
Ex.10: cured material of paste I and paste I'
Ex.11: cured material of paste J and paste J'
Ex.12: cured material of paste K and paste K'
Ex.13: cured material of paste K and paste G'
Ex.14: cured material of paste H and paste I'
Ex.15: cured material of paste M and paste M'
Ex.16: cured material of paste N and paste N'
Ex.17: cured material of paste M and paste N'
Ex.18: cured material of paste O and paste O'
Ex.19: cured material of paste N and paste O'
Ex.20: cured material of paste P and paste O'
Com. Ex. 1: cured material of paste A and paste A'
Com. Ex. 2: cured material of paste G and paste G'
Com. Ex. 3: cured material of paste L and paste L'
Com. Ex. 4: cured material of paste P and paste L'

It was confirmed from comparison between Examples 1 to 8 and Comparative Example 1, comparison between Examples 9 to 14 and Comparative Example 2, and comparison between Examples 15 to 20 and Comparative Example 3 that the dental composite resin composition into which a gold powder and/or a gold-color alloy powder is incorporated according to the present invention exhibits excellent properties of surface hardness, abrasion resistance and X-ray contrast. Further, in comparative Example 4, because of shortness of the gold-color alloy powder, substantial improvements in surface hardness and abrasion resistance were not observed, and the color tone of the cured material was not satisfactory in gold color.

A filling material prepared by using the dental composite resin composition according to the present invention had a gold-color luster like an inlay by a gold alloy and kept the gold-color luster without causing any tarnish even after lapse of 2 years in an oral cavity, and was not substantially observed to be abraded, whereby it showed excellent clinical results.

CLAIMS

1. A dental composite resin composition comprising as main components a polymerizable monomer, an inorganic filler and/or an organic filler, a gold powder and/or a gold-color alloy powder, and a polymerization catalyst.

2. A composition as claimed in claim 1, wherein the content of the said gold powder and/or gold-color alloy powder is from 1 to 60% by weight.

3. A composition as claimed in claim 1 or 2, wherein the particle size of the said gold powder and/or gold-color alloy powder is 50 μm or less.

4. A composition as claimed in any of claims 1 to 3, wherein the said gold powder and/or gold-color alloy powder is subjected to surface treatment with a silane coupling agent.

5. A composition as claimed in any of claims 1 to 4, wherein the said gold powder and/or gold-color alloy powder is selected from gold powder, gold base alloy powder, Cu-Zn base alloy powder, Cu-Al base alloy powder, In-Pd base alloy powder, Zn-Pd base alloy powder, and TiN powder.

6. A dental composite resin composition according to claim 1, substantially as described in any of the foregoing Examples 1 to 20.

Printed in the UK for HMSO, D8818935, 8/86, 7102.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.