PATENT APPLICATION FORM (CONVENTION AND NON-CONVENTION)

COMMONWEALTH OF AUSTRALIA — Regulation 9

Patents Act 1952

APPLICATION FOR A STANDARD PATENT OR A STANDARD PATENT OF ADDITION

APPLICATION ACCEPTED AND AMENDMENTS ALLOWED 24.1.90

PATENT OFFICE
A.G.P. SUB-OFFICE
--079684 $170
Collector of Public Moneys

(a) Insert full name(s) of applicant(s)

I/We (a) BAYER AKTIENGESELLSCHAFT

(b) Insert address(es) of applicant(s)

of (b) Leverkusen, Germany

(c) Delete as appropriate

hereby apply for the grant of a (c) Standard Patent ~~Patent of Addition~~ for an invention entitled (d) (METH)-ACRYLIC ACID

(d) Insert title of invention

DERIVATIVES OF TRICYCLODECANES AND THEIR USE

which is described in the accompanying (c) ~~provisional~~ complete specification.

(e) For a Convention application — details of basic application(s) —

(e) for Convention cases only

NUMBER	COUNTRY	DATE OF APPLICATION
P 35 22 006.6	GERMANY	20th June 1985

(f) For Patents of Addition only.

~~(f) For Patents of Addition (Section 72):~~

~~I/We request that the Patent may be granted as a Patent of Addition~~

~~the Patent applied for on Application No.~~ (g)

~~to~~

~~Patent No.~~ (g) ~~in the name of~~ (h)

~~I/We request that the term of the Patent of Addition be the same as that for the main invention or so much of the term of the patent for the main invention as is unexpired.~~

(g) Insert number of 'parent/main' application/or patent as appropriate.

(h) Insert name of applicant/patentee of 'parent/main' application or patent as appropriate.

I/We/Our address for service is ARTHUR S. CAVE & CO., Patent and Trade Mark Attorneys, 1 Alfred Street, Sydney, New South Wales, Australia 2000.

(i) Insert day, month and year form signed.

Dated this (i) 16th day of June, 1986

(j) Signature of applicant or Australian attorney.

BAYER AKTIENGESELLSCHAFT,
By Its Patent Attorneys,
ARTHUR S. CAVE & CO.
(Signature)

JAMES G. SIELY. F.I.P.A.A.

LODGED AT SUB-OFFICE (j)
(k) 18 JUN 1986
Sydney

(k) Seal, if any.

To:

Commissioner of Patents

ARTHUR S. CAVE & CO.
PATENT AND TRADE MARK ATTORNEYS
SYDNEY

A.S.C. — 1

PATENT DECLARATION FORM (CONVENTION)
COMMONWEALTH OF AUSTRALIA
Patents Act 1952

Regulation 12 (2)

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

To be signed by the applicant(s) or in the case of a body corporate to be signed by a person authorised by the body corporate.

In support of the Convention application made for a patent for an invention entitled

(a) Insert title of invention.

(a) (Meth)-acrylic acid derivatives of tricyclodecanes and their use

(b) Insert full name(s) of declarant(s).

I/We (b) GERHARD BUNEMANN and KLAUS DANNER , Secretaries

(c) Insert address(es) of declarant(s).

of (c) D 5090 Leverkusen, Bayerwerk, Germany

do solemnly and sincerely declare as follows:–

~~1. I am/We are the applicant(s) for the patent~~

(OR, IN THE CASE OF AN APPLICATION BY A BODY CORPORATE.)

1. I/We are authorised by BAYER AKTIENGESELLSCHAFT the applicant for the patent to make this declaration on its behalf.

2. The basic application(s) as defined by Section 141 of the Act was/were made in the following country or countries on the following date(s) namely:–

(d) Insert country in which basic application(s) was/were filed.
(e) Insert date of basic application(s).
(f) Insert full names of basic applicant(s).

in (d) Germany on (e) June 20, 1985
by (f) Bayer Aktiengesellschaft
in (d) ..... on (e) .....
by (f) .....
in (d) ..... on (e) .....
by (f) .....

~~3. I am/We are the actual inventor(s) of the invention referred to in the basic application.~~

(OR, WHERE A PERSON OTHER THAN THE INVENTOR IS THE APPLICANT)

(g) Insert full name(s) of actual inventor(s)
(h) Insert address(es) of actual inventor(s).

3. (g) 1) Jens Winkel 2) Bruno Bömer 3) Robert Schmitz-Josten 4) Gerhard Klein 5) Carlhans Süling 6) Dieter Arlt

of (h) 1) Hahnenweg 6, D 5000 Koeln 80, Germany 2) Max-Planck-Strasse 53, D 5060 Bergisch-Gladbach 2, Germany 3) Gerstenkamp 6, D 5000 Koeln 80, Germany 4) von-Flotow-Strasse 7, D 4019 Monheim, Germany 5) Carl-Leverkus-Strasse 10, D 5068 Odenthal, Germany 6) Rybniker-strasse 2, D 5000 Koeln 80, Germany

is/are the actual inventor(s) of the invention and the facts upon which the applicant(s) is/are entitled to make the application are as follows:

(i) Set out how applicant(s) derive(s) title from actual inventor(s) i.e., assignee of the invention from the actual inventor(s).

(i) The company is the Assignee of the said invention from the said inventors

4. The basic application(s) referred to in paragraph 2 of this Declaration was/were the first application(s) made in a Convention country in respect of the invention the subject of the application.

Attestation or legalization not required.

Declared at Leverkusen this 7th day of May 1986

To:

LeA 23 885-AU

The Commissioner of Patents

Signature of Declarant(s)
Gerhard Bünemann Klaus Dänner
(secretaries)

ARTHUR S. CAVE & CO.
PATENT AND TRADE MARK ATTORNEYS
SYDNEY

A.S.C.—4

(12) PATENT ABRIDGMENT (11) Document No. AU-B-58980/86
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 595209

(54) Title
DERIVATIVES OF TRICYCLODECANES AND DENTALL USE THEREOF

International Patent Classification(s)
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C08F 220/36 C08J 003/24 C08K 005/00 C07C 125/073

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3522006 20.06.85 DE FEDERAL REPUBLIC OF GERMANY

(43) Publication Date : 24.12.86

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(71) Applicant(s)
BAYER AKTIENGESELLSCHAFT

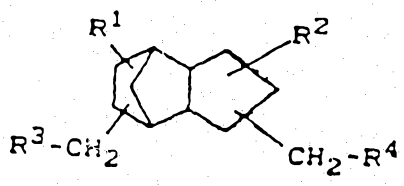
(72) Inventor(s)
JENS WINKEL; BRUNO BOMER; ROBERT SCHMITZ-JOSTEN; GERHARD KLEIN; CARLHANS SULING; DIETER ARLT

(74) Attorney or Agent
ARTHUR S. CAVE & CO.

(56) Prior Art Documents
AU 58270/86 C07C 125/073 127/15 A61K 6/08

(57) Clair

1. (Meth)-acrylic acid derivatives of tricyclodecanes of the formula



, (I)

in which

R^1 and R^2 are identical or different and denote hydrogen, lower alkyl, lower alkoxy, halogen or trifluoromethyl and

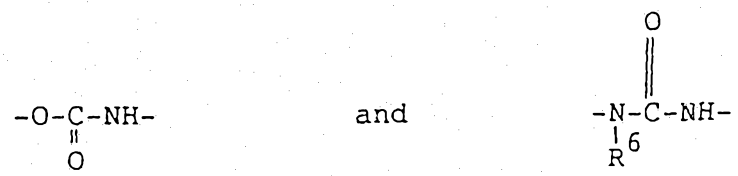
R^3 and R^4 are identical or different and represent the group

$$-X-Y-O-\underset{\underset{O}{\|}}{C}-\underset{\underset{R^5}{|}}{C}=CH_2$$

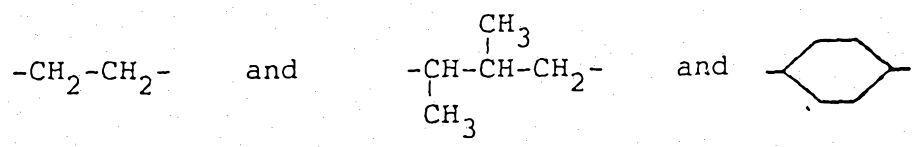
12

wherein

X denotes a divalent bridge member from the group comprising



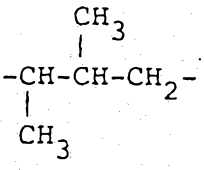
and Y denotes a divalent bridge member from the group comprising



and wherein

R^5 represents hydrogen or methyl and

R^6 represents hydrogen, lower alkyl or phenyl;

with the proviso that when R^6 is hydrogen, Y is not ethylene or  .

COMMONWEALTH OF AUSTRALIA

PATENTS ACT, 1952

Form 10
Regulation
13(2)

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE

Short Title:

Int. Cl:

595209

Application Number: 58980/86.

Lodged:

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

Complete Specification-Lodged:
Accepted:
Lapsed:
Published:

Priority:

Related Art:

TO BE COMPLETED BY APPLICANT

Name of Applicant: BAYER AKTIENGESELLSCHAFT

Address of Applicant: Leverkusen, Germany

Actual Inventor: 1.JENS WINKEL 2.BRUNO BÖMER 3.ROBERT SCHMITZ-JOSTEN 4.GERHARD KLEIN 5.CARLHANS SULING 6. DIETER ARLT

Address for Service: ARTHUR S. CAVE & CO., Patent and Trade Mark Attorneys, 1 Alfred Street, Sydney, New South Wales, Australia, 2000.

Complete Specification for the invention entitled:
(METH)-ACRYLIC ACID DERIVATIVES OF TRICYCLODECANES AND THEIR USE

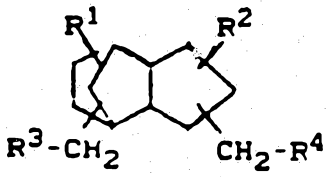
The following statement is a full description of this invention, including the best method of performing it known to me:-

ASC-49

The invention relates to new (meth)-acrylic acid derivatives of tricyclodecanes, their preparation and their use as monomers for dental materials.

Dental compositions which contain polymerisable (meth)-acrylic acid esters of tricyclodecanes are known from DE-OS (German Published Specification) 2,931,926. However, these dental compositions always show polymerization shrinkage when used.

New (meth)-acrylic acid derivatives of tricyclodecanes of the formula

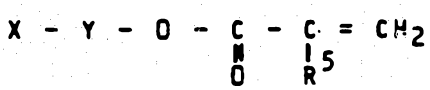


(I)

in which

R^1 and R^2 are identical or different and denote hydrogen, lower alkyl, lower alkoxy, halogen or trifluoromethyl and

R^3 and R^4 are identical or different and represent the group

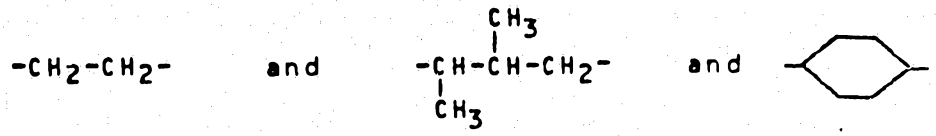


wherein

X denotes a divalent bridge member from the group comprising

and

Y denotes a divalent bridge member from the group comprising



and wherein

R^5 represents hydrogen or methyl and

R^6 represents hydrogen, lower alkyl or phenyl,

have been found.

Surprisingly, dental compositions in which (meth)-acrylic acid derivatives of tricyclodecanes according to the invention have been used as starting materials exhibit considerably less polymerisation shrinkage and are therefore particularly suitable for use in practice.

In the context of the present invention, the substituents can have the following meaning:

Lower alkyl can denote a straight-chain or branched hydrocarbon radical with 1 to about 6 carbon atoms. The following lower alkyl radicals may be mentioned as examples: methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl, isopentyl, hexyl and isohexyl. The methyl and the ethyl radical are preferred.

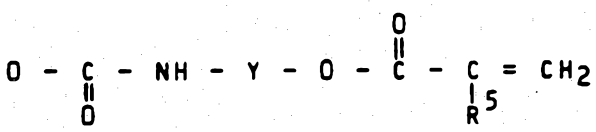
Lower alkoxy can denote a straight-chain or branched hydrocarbon radical which has 1 to about 6 carbon atoms and is bonded via oxygen. The following lower alkoxy radicals may be mentioned as examples: methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, pentoxy, isopentoxy, hexoxy and isohexoxy. The methoxy and the ethoxy radical are preferred.

Halogen can denote fluorine, chlorine, bromine and iodine. Fluorine and chlorine are preferred.

Preferred (meth)-acrylic acid derivatives of tricyclodecanes of the formula I are those in which

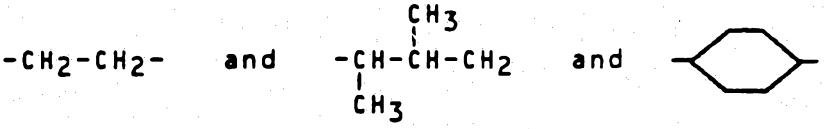
R^1 and R^2 denote hydrogen,

R^3 and R^4 are identical or different and represent the group



wherein

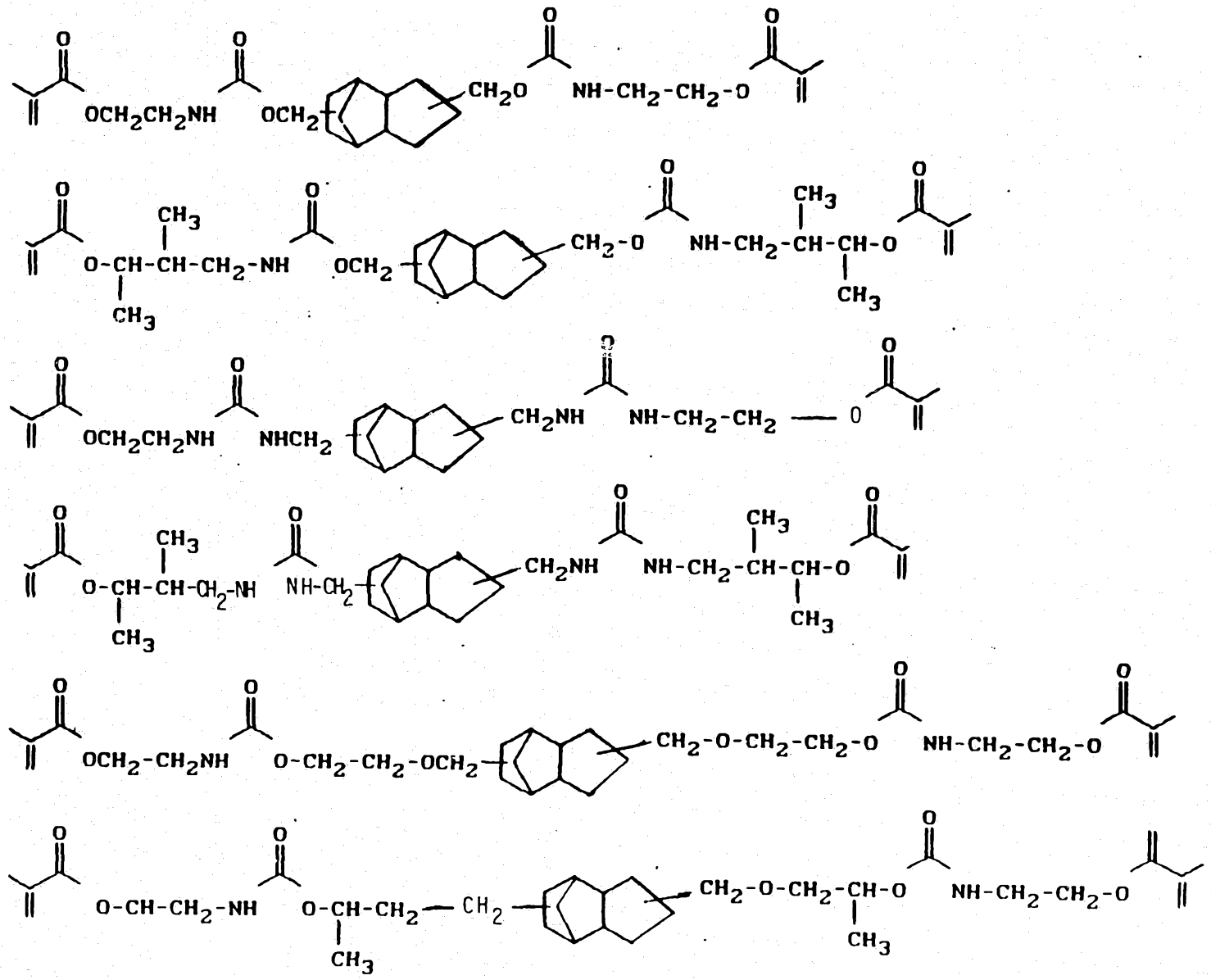
Y denotes a divalent bridge member from the group comprising



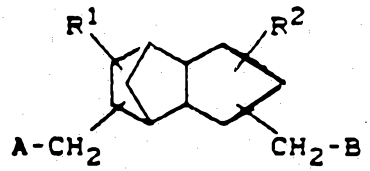
and wherein

R^5 represents hydrogen or methyl.

The following (meth)-acrylic acid derivatives of tricyclodecanes may be mentioned as examples:



A process has also been found for the preparation of (meth)-acrylic acid derivatives of tricyclodecanes, which is characterized in that tricyclodecanes of the formula



(II)

in which

R^1 and R^2 are identical or different and denote hydrogen, lower alkyl, lower alkoxy, halogen or trifluoromethyl and

A and B are identical or different and denote hydroxyl or the radical $-NHR^6$,

wherein

R^6 represents hydrogen, lower alkyl or phenyl,

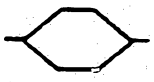
are reacted with (meth)-acrylic acid ester-isocyanates of the formula

$$CH_2 = \underset{\underset{R^5}{|}}{C} - \underset{\underset{O}{\|}}{C} - Y - NCO \qquad (III)$$

in which

R^5 represents hydrogen or methyl and

Y denotes a divalent bridge member from the group comprising

$-CH_2-CH_2-$ and $-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_2$ and 

if appropriate in an inert solvent in the presence of a catalyst in the temperature range from 0 to 100°C.

The dihydroxymethyltricyclodecanes employed as starting compounds are known per se (literature: U.S. Patent 4,131,729), and they can be prepared, for example, by reac-

tion of dicyclopentadiene, formaldehyde and hydrogen.

The diaminomethyltricyclodecanes employed as starting compounds are known per se and can be prepared, for example, by reaction of tosylates with ammonia.

(Meth)-acrylic acid ester-isocyanates are known from DE-OS (German Published Specification) 3,338,077 and can be prepared, for example, by phosgenation of dihydrooxanines.

It is possible to carry out the process according to the invention without solvents.

Inert solvents for the process according to the invention are preferably polar solvents which do not change under the reaction conditions. Preferred solvents are, in particular, chloroform, tetrahydrofuran, dioxane, methylene chloride, toluene, acetonitrile and freon. Particularly preferred solvents are chloroform, tetrahydrofuran, freon and acetonitrile.

In a particular embodiment, the process according to the invention is carried out with the exclusion of water. A maximum amount of water of less than 0.1% is particularly preferred.

Catalysts for the process according to the invention are in general metal salts of higher fatty acids. Examples of preferred catalysts are dibutyl-tin laurate or tin(II) octoate. However, compounds with tertiary amino groups, such as pyridine, methylpyridine, N,N'-dimethylpiperazine and N,N-dimethylbenzylamine, and titanium compounds are also preferred.

The catalyst is in general employed in an amount of 0.01 to 2.5% by weight, preferably 0.1 to 1.5% by weight, based on the total amount of the reactants.

In a preferred embodiment, the process according to the invention can be carried out in the presence of a polymerization inhibitor. A polymerization inhibitor can be, for example, 2,6-di-tert.-butyl-4-methylphenol. However, it is also possible to use oxygen as the polymerization inhibitor. In this case, oxygen is passed into the

reaction mixture. In general, atmospheric oxygen is sufficient.

The polymerization inhibitor is in general employed in an amount of 0.01 to 0.2% by weight, preferably 0.05 to 0.1% by weight.

The tricyclodecanes of the formula II are in general employed in an amount of 0.8 to 1.4 moles, preferably 0.8 to 1.2 moles, per 2 moles of the (meth)-acrylic acid ester-isocyanates.

The process according to the invention is in general carried out in the temperature range from 0 to 100°C, preferably 30 to 70°C. The process according to the invention is in general carried out under normal pressure. However, it is also possible to carry out the process according to the invention under reduced or increased pressure (for example in the pressure range from 0.1 to 10 bar).

The process according to the invention can be carried out, for example, as follows:

The reactants are dissolved in the solvent, and the catalyst and, if appropriate, the polymerization inhibitor are added, with stirring. The course of the reaction with respect to time can be monitored, for example, by measurement of the IR spectra. When reaction of the isocyanate groups is complete, the reaction products are isolated by removing the solvent. Prior purification with the aid of absorbents, for example active charcoal, bleaching earth, silica gel or aluminum oxide, is possible.

The (meth)-acrylic acid derivatives of tricyclodecanes according to the invention can be used as monomers for dental materials. Thus, it is possible to employ them as monomers for polymeric dental filling compositions or coating agents (dental lacquers) in the dental field.

For use as monomers for polymeric dental filling compositions or coating agents in the dental field, the (meth)-acrylic acid derivatives of tricyclodecanes accord-

ing to the invention can be mixed with monomers which are known per se, for example in order to adapt the viscosity to suit the intended use. Viscosities in the range from 60 to 10,000 mPas are preferred here. This can be achieved, if appropriate, by admixing a comonomer of low viscosity to the monomers according to the invention, as a reactive diluent. The compounds according to the invention are employed in the mixture with comonomers in an amount of about 30 to about 90% by weight, an amount of 50 to 85% by weight being particularly preferred.

In the context of the present invention, it is likewise preferable to employ mixtures of different (meth)-acrylic acid derivatives of tricyclodecanes according to the invention.

It is also possible to employ monomer mixtures which contain several comonomers as reactive diluents.

The following comonomers may be mentioned as examples: triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, 1,12-dodecanediol dimethacrylate, 1,6-hexanediol dimethacrylate, diethylene glycol dimethacrylate, 2,2-bis-[p-(2'-hydroxy-3'-methacrylolyloxyprop-oxy)-phenyl]-propane, 2,2-bis-[p-(2'-methacrylolyloxyethoxy)-phenyl]-propane, trimethylol-propane tri-(meth)-acrylate and bis-(meth)-acrylolyloxyethoxymethyl-tricyclo-[5.2.1. $O^{2.6}$]-decane (DE-OS (German Published Specification) 2,931,925 and DE-OS (German Published Specification) 2,931,926).

Comonomers which have a boiling point above 100°C under 13 mbar are particularly preferred.

The (meth)-acrylic acid derivatives of tricyclo-decanes according to the invention, if appropriate mixed with the comonomers mentioned, can be hardened by methods which are known per se to give crosslinking polymers (Am. Chem.Soc., Symp.Ser. 212, 359-371 (1983)). A system of a peroxidic compound and a reducing agent, for example based on tertiary aromatic amines, is suitable for the so-called

redox polymerization.

Examples of peroxides are: dibenzoyl peroxide, dilauryl peroxide and di-4-chlorobenzoyl peroxide.

Examples which may be mentioned of tertiary aromatic amines are N,N-dimethyl-p-toluidine, bis-(2-hydroxyethyl)-p-toluidine, bis-(2-hydroxyethyl)-3,5-dimethylaniline and N-methyl-N-(2-methyl-carbamoyloxypropyl)-3,5-dimethylaniline (German Patent Specification 2,759,239).

The concentrations of the peroxide and of the amine are advantageously chosen such that they are 0.1 to 5% by weight, preferably 0.5 to 3% by weight, based on the monomer mixture. The monomer mixtures containing peroxide and amine are stored separately until used.

The monomers according to the invention can also be brought to polymerization by irradiation with UV light or visible light (for example in the wavelength range from 230 to 650 nm). Examples of suitable initiators for the photoinitiated polymerization are benzil, benzil dimethyl ketal, benzoin monoalkyl ethers, benzophenone, p-methoxybenzophenone, fluorenone, thioxanthone, phenanthrenequinone and 2,3-bornanedione (camphorquinone), if appropriate in the presence of photoactivators with a synergistic action, such as N,N-dimethylaminoethyl methacrylate, triethanolamine or 4-N,N-dimethylaminobenzenesulphonic acid diallylamide. The procedure for the photopolymerization process is described, for example, in German Patent Specification 3,135,115.

In addition to the initiators described above, light stabilizers and stabilizers known per se for this intended use can be added to the (meth)-acrylic acid derivatives of tricyclodecanes according to the invention.

Light stabilizers are described, for example, in (Grächter, Müller: Kunststoff-Additive (Plastics Additives), 2nd edition, Carl Hauser Verlag, Munich, Vienna). The following light stabilizers may be mentioned as examples: Cyasorbuva®, Tinuvin P®, Tinuvin 770®, Tinuvin 622® and

Tinnvin 765®.

Stabilizers are described, for example, in (Ullmanns Encyclopädie der technischen Chemie (Ullmann's Encyclopaedia of Industrial Chemistry), Verlag Chemie Weinheim, 4th edition, Volume 8). The following stabilizers may be mentioned as examples: 2,6-di-tert.-butylphenol, 2,6-di-tert.-butyl-4-methylphenol, 2,6-di-octadecyl-4-methylphenol, 1,1'-methylene-bis-(naphth-2-ol) and the like.

The light stabilizer and the stabilizer are in each case in general employed in an amount of 0.01 to 0.50 parts by weight per 100 parts by weight of the monomer mixture.

The monomer mixtures can be employed, without the addition of fillers, as coating agents (dental lacquers).

When used as dental filling compositions, fillers are in general added to the monomer mixtures obtained. Monomer mixtures which have a viscosity in the range from 60 to 10,000 mPas are particularly advantageous, in order to achieve a high degree of filling.

Inorganic fillers are preferably admixed to the monomer mixtures containing the compounds according to the invention. Examples of inorganic fillers which may be mentioned are rock crystal, graphite, cristoballite, quartz glass, highly disperse silicic acid, aluminium oxide and glass ceramics, for example glass ceramics containing lanthanum and zirconium (DE-OS (German Published Specification) 2,347,501).

The inorganic fillers are preferably pretreated with an adhesion promoter to improve the bonding to the polymer matrix, for example of a polymethacrylate. Adhesion promotion can be achieved, for example, by treatment with organosilicon compounds (Progress in Organic Coatings 11 297-308 (1983)). 3-Methacrylolyloxipropyltrimethyloxysilane is preferably employed.

The fillers for the dental filling compositions

according to the invention in general have an average particle diameter of 0.01 to 100 µm, preferably 0.05 to 50 µm and particularly preferably 0.05 to 5 µm. It may also be advantageous to employ several fillers of different particle diameter side by side.

The filler content in the dental filling composition is in general 5 to 85% by weight, preferably 50 to 80% by weight.

For the preparation of the dental filling compositions, the components are processed using commercially available kneading machines.

The content of (meth)-acrylic acid derivatives of tricyclodecanes according to the invention in the filling compositions is in general 5 to 85% by weight, preferably 15 to 50% by weight, based on the filling composition.

Dental materials based on the (meth)-acrylic acid derivatives of tricyclodecanes according to the invention have, surprisingly, a low polymerization shrinkage and a high mechanical strength.

Preparation Examples:

1) Reaction of 3(4),8(9)di-hydroxymethyl-tricyclo-[5.2.1.$0^{2,6}$]-decane with 2-isocyanatoethyl methacrylate

0.3 mole of 3(4),8(9)di-hydroxymethyl-tricyclo-[5.2.1.$0^{2,6}$]-decane, 0.6 mole of 2-isocyanatoethyl methacrylate, 0.2 g of dibutyl-tin dilaurate and 50 mg of 2,6-di-tert.-butyl-4-methyl-phenol (Ionol) are reacted in a suitably equipped reaction vessel in the course of 3 hours at 70°C, while stirring and passing through dry air.
151 g of a colourless, slightly viscous liquid are obtained.

^{1}H-NMR (ppm) in $CDCl_3$/TMS: 0.75-2.70 (14 H); 1.95 (4H), 3.30-3.60 (4H); 3.70-3.95 (4H), 4.10-4.30 (4H); 50-530 (2H); 5.50-5.65 (2H) and 6.08-6.15 (2H)
Viscosity (25°C): 885 Pas

2) Reaction of 3(4),8(9)di-hydroxymethyl-tricyclo-[5.2.1.$0^{2,6}$]-decane with 1-isocyanato-2-methyl-but-3-yl acrylate

0.25 mole of 3(4),8(9)-dihydroxymethyl-tricyclo-[5.2.1.$0^{2,6}$]-decane, 0.5 mole of 1-isocyanato-2-methyl-but-2-yl acrylate, 0.2 g of dibutyl-tin dilaurate and 50 mg of Ionol are reacted as described in 1.

^{1}H-NMR (ppm) in $CDCl_3$/TMS: 0.85-1.05 (6H), 1.15-1.35 (6H), 0.75-2.70 (14H), 2.70-3.55 (4H), 3.70-3.95 (4H), 4.70-5.30 (4H) and 5.70-6.55 (6H)

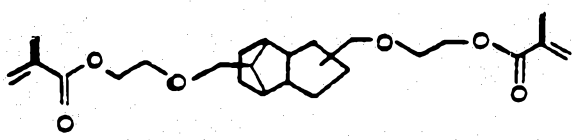
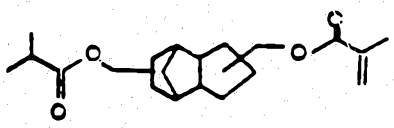
Viscosity (25°C): 1,220 Pas

Use Examples

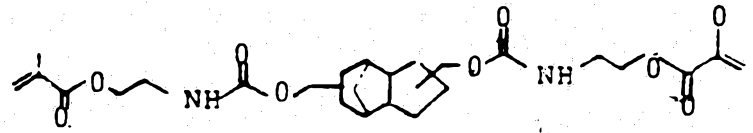
3) Measurement of the polymerization shrinkage:

2% of benzoyl peroxide is dissolved in the pure monomer. 5 g of this solution are introduced into a cylindrical glass vessel of 3 cm diameter and covered with a layer of nitrogen. The solution is heated at 80°C for 1 hour and at 130°C for 15 minutes, whereupon the monomers polymerize. The density of the resulting test pieces is determined and the polymerization shrinkage is determined by comparison with the density of the liquid monomers.

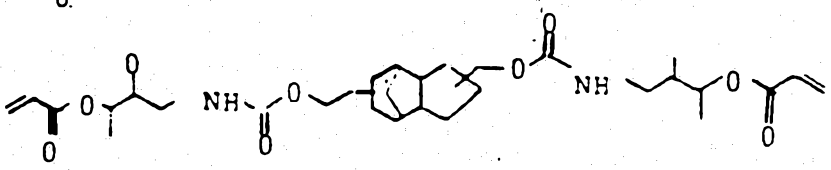
Table I

Monomer of the comparison experiments	Polymerization shrinkage
	
(DE-OS (German Published Specification) 2,931,926)	7.3%
	
(DE-OS (German Published Specification) 2,816,823)	7.7%

Monomers according to the invention



6.1%



5.7%

4) Composition for filling hollow dental cavities

a) Redox-hardening system

Peroxide paste

2% of benzoyl peroxide is dissolved in a mixture of 70 parts of monomer from 1 and 30 parts of triethylene glycol dimethacrylate.

10 g of silanized radicals glass ceramic are processed with 4 g of this solution to give a paste.

Amine paste

1.4% of N-methyl-N-β-(methylcarbamyloxy)-propyl-3,5-dimethylaniline are dissolved in a mixture of 70 parts of monomer from 1 and 30 parts of triethylene glycol dimethacrylate.

4 g of this solution are processed with 10 g of silanized glass ceramic to give a paste.

If equal parts of amine paste and peroxide paste are mixed with one another, the mixture hardens in 2 minutes. The pastes can be coloured with pigment and are suitable for filling hollow dental cavities.

b) Photo-hardening system

0.5% of N,N-diallyl-p-dimethylaminobenzenesulphonic acid amide, 0.2% of camphorquinone and 0.125% of 4-N,N-dimethylaminobenzenesulphonic acid diallylamide are dissolved in a mixture of 70 parts of monomer from 1 and 30 parts of triethylene glycol dimethacrylate. 10 g of silanized glass ceramic are processed with 4 g of this solution to give a paste. If this composition is irradiated with a commercially available dental lamp (Translux, Kulzer), a layer of

7.9 mm has hardened completely after 40 seconds.

5) Preparation of sealer solutions

a) Redox-hardening system

Catalyst solution

2% of benzoyl peroxide are dissolved in a mixture of 10 parts of triethylene glycol dimethacrylate and 90 parts of monomer from 2.

Activator solution

2% of N-methyl-N- -(methylcarbamoyloxy)-propyl-3,5-dimethylaniline are dissolved in a mixture of 10 parts of triethylene glycol dimethacrylate and 90 parts of monomer from 2.

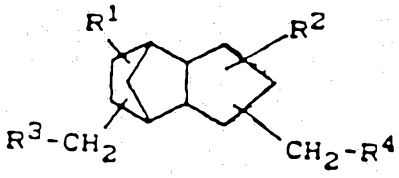
A mixture of equal parts of catalyst solution and activator solution hardens in 1 minute 15 seconds.

6) Photo-hardening sealer

0.5% of N,N-diallyl-p-dimethylaminobenzenesulphonic acid amide, 0.2% of camphorquinone and 0.125% of benzil dimethyl ketal are dissolved in the monomer from 1. On irradiation with a commercially available dental lamp (Translux, Kulzer), the liquid hardens to a solid film.

The claims defining the invention are as follows:

1. (Meth)-acrylic acid derivatives of tricyclodecanes of the formula

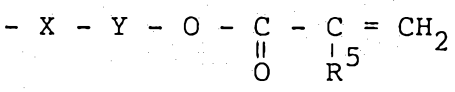


(I)

in which

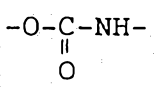
R^1 and R^2 are identical or different and denote hydrogen, lower alkyl, lower alkoxy, halogen or trifluoromethyl and

R^3 and R^4 are identical or different and represent the group

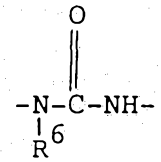


wherein

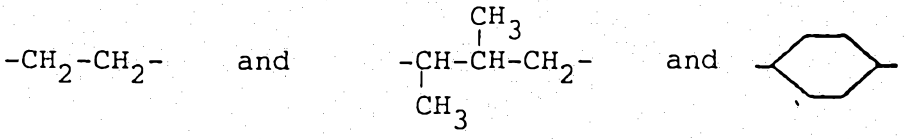
X denotes a divalent bridge member from the group comprising



and



and Y denotes a divalent bridge member from the group comprising



and wherein

R^5 represents hydrogen or methyl and

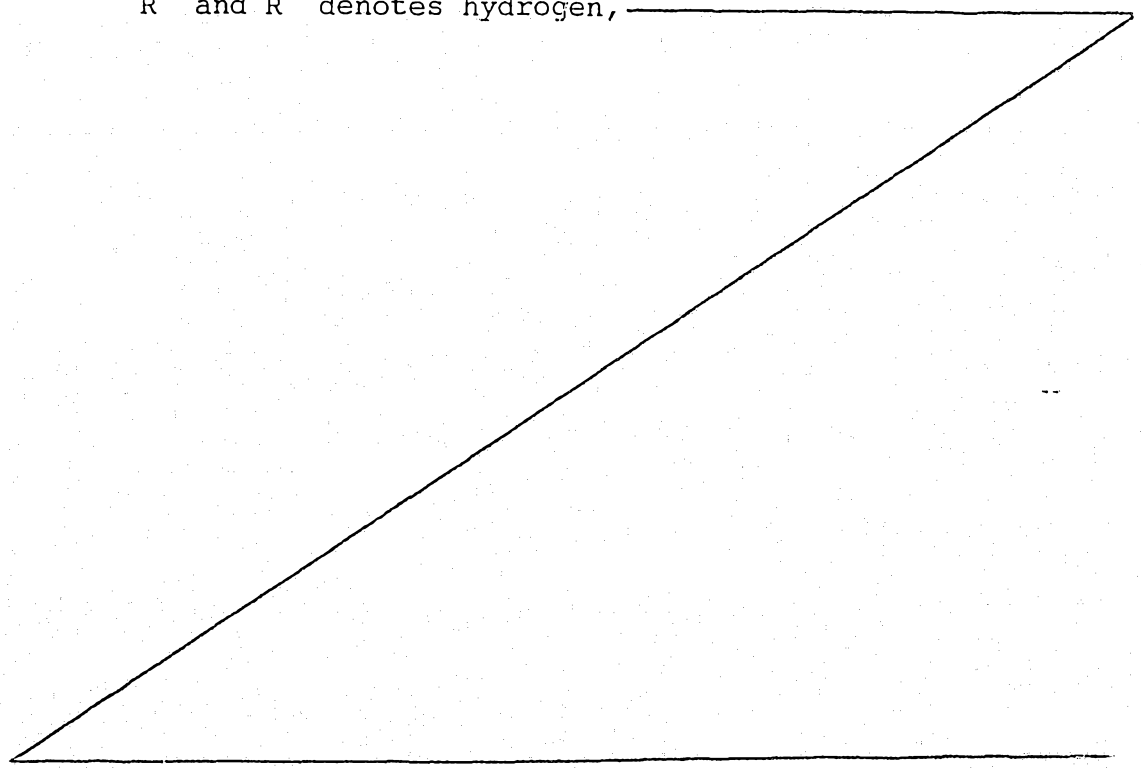
R^6 represents hydrogen, lower alkyl or phenyl;

with the proviso that when R^6 is hydrogen, Y is not ethylene or $-CH(CH_3)-CH(CH_3)-CH_2-$.

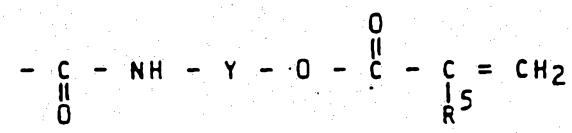
2. (Meth)-acrylic acid derivatives of tricyclodecanes according to Claim 1,

wherein

R^1 and R^2 denotes hydrogen,

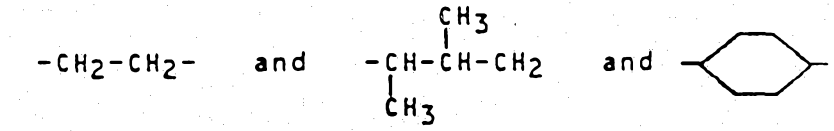


R^3 and R^4 are identical or different and represent the group



wherein

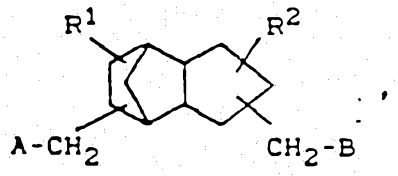
Y denotes a divalent bridge member from the group comprising



and wherein

R^5 represents hydrogen or methyl.

3. Process for the preparation of (meth)-acrylic acid derivatives of tricyclodecanes according to Claim 1, characterized in that tricyclodecanes of the formula



in which

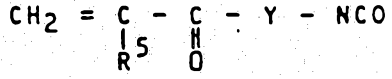
R^1 and R^2 are identical or different and denote hydrogen, lower alkyl, lower alkoxy, halogen or trifluoromethyl and

A and B are identical or different and denotes hydroxyl or the radical $-NHR^6$,

wherein

R^6 represents hydrogen, lower alkyl or phenyl,

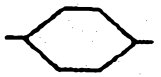
are reacted with (meth)-acrylic acid ester-isocyanates of the formula



in which

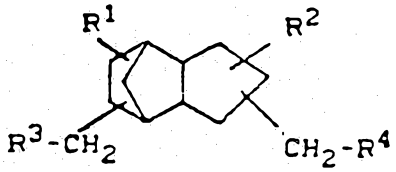
R^5 represents hydrogen or methyl and

Y denotes a divalent bridge member from the group comprising

$-CH_2-CH_2-$ and $-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_2-$ and 

if appropriate in an inert solvent in the presence of a catalyst in the temperature range from 0 to 100°C.

4. Polymer formed from (meth)-acrylic acid derivatives of tricyclodecanes of the formula



in which

R^1 and R^2 are identical or different and denote hydrogen, lower alkyl, lower alkoxy, halogen or trifluoromethyl and

R^3 and R^4 are identical or different and represent the group

$$-X-Y-O-\underset{\underset{O}{\|}}{C}-\underset{\underset{R^5}{|}}{C}=CH_2$$

wherein

X denotes a divalent bridge member from the group comprising

$-O-\underset{\underset{O}{\|}}{C}-NH-$ and $-N(\underset{\underset{R^6}{|}}{\ })-\underset{\underset{O}{\|}}{C}-NH-$

and Y denotes a divalent bridge member from the group comprising

$-CH_2-CH_2-$ and $-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_2-$ and 

and wherein

R^5 represents hydrogen or methyl and

R^6 represents hydrogen, lower alkyl or phenyl;

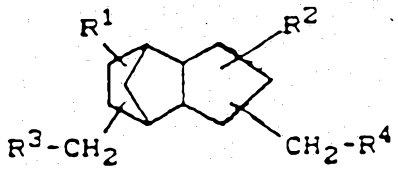
with the proviso that when R^6 is hydrogen, Y is not ethylene or $-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_2-$.

5. Monomers of (Meth)-acrylic acid derivatives of tricyclodecanes according to Claim 1 when used in the dental field.

6. Method according to Claim 5, characterized in that monomers of (meth)-acrylic acid derivatives of tricyclodecanes are employed in dental filling compositions.

7. Method according to Claim 5, characterized in that monomers of (meth)-acrylic acid derivatives of tricyclodecanes are used in coating agents for teeth.

8. Dental filling compositions, characterized in that they contain monomers of (meth)-acrylic acid derivatives of tricyclodecanes of the formula



in which

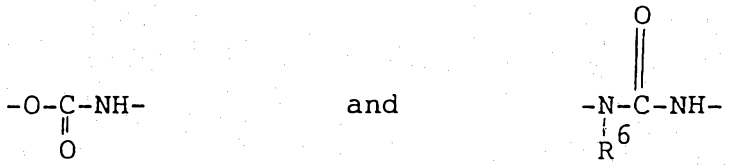
R^1 and R^2 are identical or different and denote hydrogen, lower alkyl, lower alkoxy, halogen or trifluoromethyl and

R^3 and R^4 are identical or different and represent the group

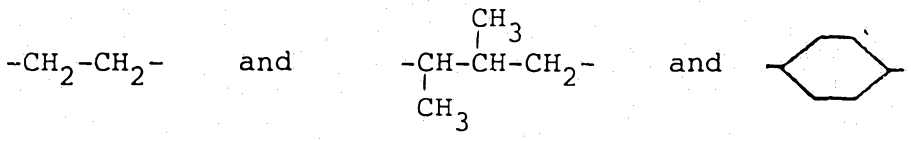
$$-X-Y-O-\underset{\underset{O}{\|}}{C}-\underset{\underset{R^5}{|}}{C}=CH_2$$

wherein

X denotes a divalent bridge member from the group comprising



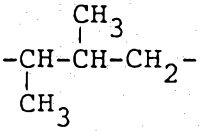
and Y denotes a divalent bridge member from the group comprising



and wherein

R^5 represents hydrogen or methyl and

R^6 represents hydrogen, lower alkyl or phenyl;

with the proviso that when R^6 is hydrogen, Y is not ethylene or  .

9. Dental filling compositions according to Claim 8, characterized in that, in addition to (meth)-acrylic acid derivatives of tricyclodecanes, they contain another comonomer.

DATED this 12th day of January, 1990.

BAYER AKTIENGESELLSCHAFT
By Its Patent Attorneys
ARTHUR S. CAVE & CO.

0140g/AMR