(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
8 February 2007 (08.02.2007)

PCT

(10) International Publication Number
WO 2007/016295 A1

(51) International Patent Classification:
C08L 71/02 (2006.01) *C08K 5/36* (2006.01)

(21) International Application Number:
PCT/US2006/029311

(22) International Filing Date: 27 July 2006 (27.07.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
05016531.5 29 July 2005 (29.07.2005) EP

(71) Applicant *(for all designated States except US)*: **3M INNOVATIVE PROPERTIES COMPANY** [US/US]; 3m Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **KLETTKE, Thomas** [DE/DE]; Espe Platz, D-82229 Seefeld (DE). **FÜHRER, Cornelia** [DE/DE]; Schimmelreiterweg 4, D-87497 Wertach (DE). **HAILAND, Andrea** [DE/DE]; Espe Platz, D-82229 Seefeld (DE). **MIKULLA, Markus** [DE/DE]; Espe Platz, D-82229 Seefeld (DE).

(74) Agents: **EDMAN, Sean J.** et al.; 3M Center, Office Of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

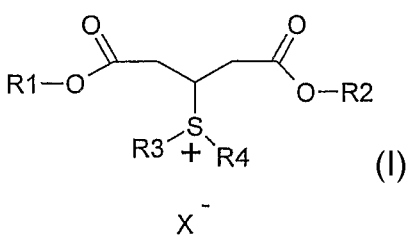
(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2007/016295 A1

(54) Title: SULFONIUM INITIATORS, PROCESS FOR PRODUCTION AND USE IN CATIONIC POLYMERIZABLE COMPOSITIONS



(I)

(57) Abstract: The invention relates to an initiator comprising at least one structural element characterized by the following formula (I) wherein X^- is a non or low coordinating anion, R1, R2, R3, R4 are independently linear, cyclic or branched C_1 - C_{20} alkyl or alkylene groups, wherein one or more of the methylene groups contained in the alkyl or alkylene group can be substituted by - CO-, -CONH-, -CON(CH_3)-, -S- and/or -0-, and wherein R1 , R2, R3 and/or R4 can act as a bridging element connecting two or more structural elements. The invention is also related to a process of producing the initiator and to a curable composition comprising the initiator, a process for producing the curable composition a kit comprising a cationically curable composition and the inventive initiator and the use of the initiator or the curable composition comprising the initiator for various applications, especially in the dental field.

Sulfonium Initiators, Process for Production and Use in Cationic Polymerizable Compositions

The invention relates to a new class of initiators, a process for producing them, a cationic curable composition containing them and the use of the initiator and the composition, e.g. in the dental field.

BACKGROUND OF THE INVENTION

Rubber elastic compositions containing aziridine compounds are know for a long time. Curing of these compositions is usually effected using specific catalysts.

In this respect US 4,167,618 A1 describes a process for the polymerization of aziridine compounds. The polymerization process includes mixing an aziridine compound with an alkyl sulfonium salt initiator having at least one hydrogen atom and an electron attracting radical in the carbon atom of the alkyl group in β-position in regard to the sulphur atom.

WO 01/17483 A1 relates to elastomer materials based on N-alkyl aziridine compounds comprising a base constituent, which contains aziridine compounds, and comprising a catalyst constituent, which contains at least one acidically active compound, whereby both constituents are mixed before use. The elastomer materials are characterized in that one or more boric acid complexes are used as an acidically active compound of the catalyst constituent. The elastomer materials can be used as dental impression material, bite recording material, and duplicating material.

In DE 19 753 456 A1 a two-component cationically-curable aziridine polyether-based composition is described, comprising a catalyst component, including acid(s) and aziridine salt(s) of an acid, and a base component including a mixture of N-alkylaziridine polyol ethers and a cationic polymerization retarding agent(s).

US 2003/153726 A1 relates to catalyst components containing at least one Brönsted acid, water and at least one antacid-acting compound. The catalyst components can be used to initiate cure of an aziridino-group-containing material.

Depending on the intended use, in the dental field the materials usually have different viscosities (light body, medium body, heavy body). In view of the fact that sometimes relatively large amounts of conventional alkyl sulfonium salt initiators are needed to cure aziridine polyether-based compositions, the viscosity of the components of the

composition may need to be adjusted to ensure adequate mixing and application of the mixed paste.

SUMMARY OF THE INVENTION

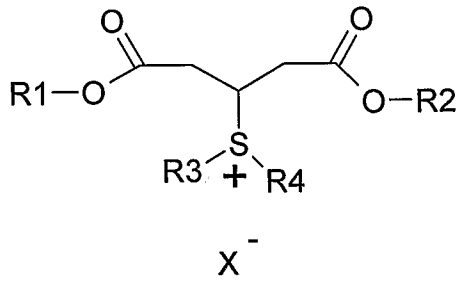
Thus, there is a need for a new initiator, which can be used for curing a cationically polymerizable composition.

It would be an advantage, if the new initiator can be manufactured in an easy and inexpensive manner.

It would be a further advantage, if adding the initiator to a paste allows adjustment of the rheology (e.g. viscosity) of this paste.

It has been found that one or more of the above mentioned objects can be achieved by providing an initiator as described in the text and claims below.

In one aspect, the invention provides an initiator comprising at least one structural element of the following formula I



wherein

X^- is a non or low coordinating anion,

R1, R2, R3 and R4 are independently linear, cyclic or branched $C_1 - C_{20}$ alkyl or alkylene groups, wherein one or more of the methylene groups may be substituted by –CO- , -CONH-, -$CON(CH_3)$-, -S- and/or –O-,

and wherein R1, R2, R3 and/or R4 can act as a bridging element, connecting two or more structural elements.

Subject to the question whether bridging elements are present or not, the initiator can be characterized as monomer, dimer, trimer, higher oligomer or polymer with one, two, three, four or more sulfonium groups.

In another aspect, this invention provides a process of producing the initiator, curable compositions comprising the initiator, a process for producing the curable compositions, a kit comprising a cationically curable composition and the inventive initiator and the use of the initiator or the curable composition comprising the initiator for various applications, especially in the dental field.

The terms "comprises" and variations thereof do not have a limiting meaning where these terms appear in the description and claims.

As used herein, "a," "an," "the," "at least one," and "one or more" are used interchangeably. Thus, for example, a dental composition that comprises "a" oxirane-containing monomer can be interpreted to mean that the dental composition includes "one or more" oxirane-containing monomers. Similarly, a composition comprising "a" filler can be interpreted to mean that the composition includes "one or more" types of fillers.

Also herein, the recitations of numerical ranges by endpoints include all numbers subsumed within that range (e.g., 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, 5, etc.).

The term “non or low coordinating group” within the meaning of the invention are anions of strong acids, preferably acids having a pKs value below about 2. Respective examples are BF_4^-, $CF_3SO_3^-$, SbF_6^-, AsF_6^- or 2,5-di-chloro-benzolsulfonate, but even other low coordinating anions can be used.

The term “bridging element” within the meaning of the invention is defined as a chemical group being able to connect two or more of the aforementioned structural elements comprising at least one sulfonium group.

The term “sulfonium equivalent weight” or ““Eq” within the meaning of the invention is calculated as molecular mass of the initiator divided by the number of sulfonium groups present in the initiator. In regard to oligomers or polymers the calculation of the sulfonium equivalent weight is based the Eq of one repeating unit.

The term “dental materials” comprises impression materials, such as precision impression materials, situation impression materials, bite registration materials, duplicating materials (applicable for the duplication of master models, e.g. for all-ceramic restorations requiring

a refractory investment model and when inlays, onlays, cantilevers and other precision attachments are being fabricated) and modelling materials (applicable for e.g. reconstructing the gingival, producing crowns and bridges). Duplicating and modelling materials are commercially available e.g. from 3M ESPE AG under the trademarks Reprogum™ or Vestogum™.

The term "cationically polymerizable compound" within the meaning of the invention is defined as a compound which can be polymerised using an initiator containing or being able to produce cations.

The term "glutaconate" within the meaning of the invention comprise the free glutaconic acid, the partly or de-protonated form of the glutaconic acid (salt of the acid) or an ester (mono-or di-ester) thereof or combinations of glutaconic acid, partly or de-protonated species or esters.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

R1, R2, R3 and R4 are independently linear, cyclic or branched $C_1 - C_{20}$ alkyl or alkylene groups, wherein one or more of the methylene groups may be substituted by –CO- , -CONH-, -CON(CH_3)-, -S- and/or –O-.

Representative examples of R1 or R2 of the formula of the inventive initiators are methyl, ethyl, n-propyl, 2-propyl, n-butyl, sec-butyl, tert.-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl groups and the like. One or more methylene groups contained in the alkyl or alkylene groups of R1 and R2 (e.g. 2, 3, 4 5 or 6) may be substituted by –CO- , -CONH-, -CON(CH_3)-, -S- and/or –O-. In preferred examples of the initiator, R1 and R2 are the same and are selected from $C_4 - C_8$ alkyl groups like n-butyl, n-pentyl, n-hexyl, n-heptyl or n-octyl groups.

Preferred R3 groups may be a substituted or not substituted linear or branched alkyl groups. Representative examples of preferred R3 groups are methyl, ethyl, n-propyl, 2-propyl, n-butyl, sec-butyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, and other alkylgroups up to about 20 carbon atoms.

Preferred R4 groups may be substituted or unsubstituted linear or branched alkyl groups. Examples of preferred R4 groups are alkyl group like octyl, nonyl, decyl, undecyl and dodecyl. One ore more of the methylene groups (e.g. 2, 3, 4 5 or 6) of this alkyl chain may be substituted by –CO- , -CONH-, -CON(CH_3)- - S- and/or –O-. Some specific

examples of preferred R4 groups are $CH_2CH_2COOCH_2CH_2CH_2CH_3$, CH_2CH_2COO-isooclylester, $CH_2COOCH_2CH_2CH_2CH_3$.

Bridging elements can be introduced by reacting the carbonic acid ester group(s) of a precursor of the inventive initiator with a diol containing e.g. 2 to 20 carbon atoms in a polycondensation reaction. By doing so, a polycondensed product can be provided containing as repeating unit the structural element comprising at least one sulfonium group as defined in the formula above. This kind of modification can be used e.g. for adjusting the molecular weight of the initiator and by doing so even the viscosity of a composition containing the initiator can be adjusted.

Further bridging elements can be introduced by reacting the carbonic acid ester group(s) of the precursor of the inventive initiator with tri-, tetra- or higher functional polyols. In these cases an excess of the precursor should be used to avoid a crosslinking reaction.

As mentioned above R1, R2, R3 and R4 can independently function as a bridging element to another structural element comprising a sulfonium group. E.g. a moiety like -$(CH_2)_8$-, -$(CH_2)_6$- or -$(CH_2)_4$- may connect two structures containing a sulfonium group. For oligomers or polymers end groups like methyl esters or ethyl esters are preferred, but even higher ester groups up to 20 C-atoms can be advantageous. However, it is also possible to introduce other bridging groups e.g. using dithiols for the synthesis.

Preferred embodiments of the initiator can be characterized as polycondensable if they comprise reactive groups able to undergo polycondensation reactions resulting in an increase of the molecular weight such as trans-esterification reactions

Typically, the initiator will have a molecular weight (MW) in the range of about 300 to about 25,000 g/mol, preferably, in the range of about 400 to about 20,000 g/mol, or more preferably, in the range of about 500 to about 10,000 g/mol, wherein the molecular weight (MW) of oligomers and polymers is the number average molecular weight (Mn)

Typical sulfonium equivalent weights (Eq) for the initiator can be in the range of about 300 to about 800 g/mol, and preferably in the range of about 350 to about 750.

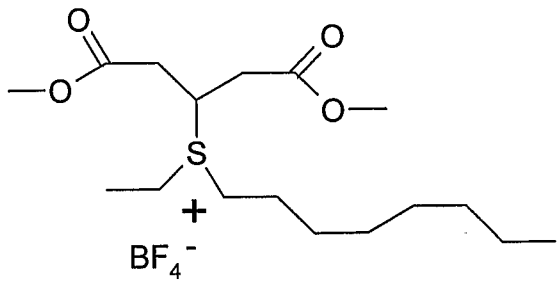
The initiators are typically oily or solid at ambient conditions (23°C, 1013 mbar), oily initiators are preferred. If the initiator is a solid substance, the melting point is usually below about 50 °C.

The initiators can be dissolved in a variety of different solvents. Solvents having no bitter taste are preferred. Examples of suitable solvents include, e.g. ,citrates such as acetyl tri-n-butyl citrate (CAS 77-90-7), acetyl tri-n-hexyl citrate (CAS 2481792-3) or acetyl tri-2-

ethylhexyl citrate (CAS 144-15-0). Especially preferred are the last two solvents because they can generally dissolve the inventive initiators at ambient conditions and they do not taste bitter.

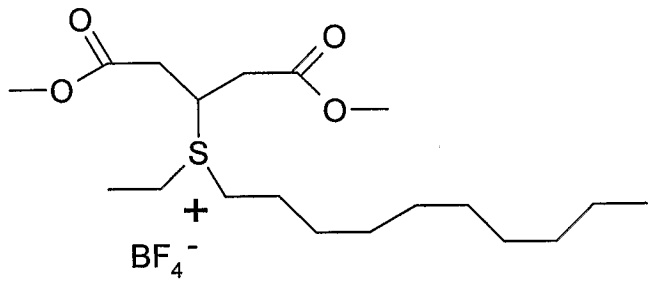
Respective examples of initiators according to the invention are given below:

Example 1 / Initiator - 1:



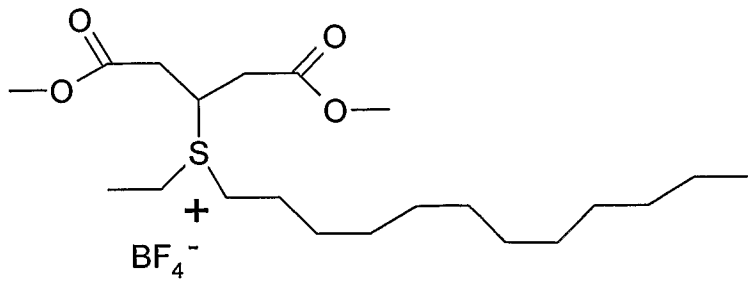
Molecular weight (MW) = 420.32 g; Equivalent Eq = 420.32 g

Example 2 / Initiator - 2:



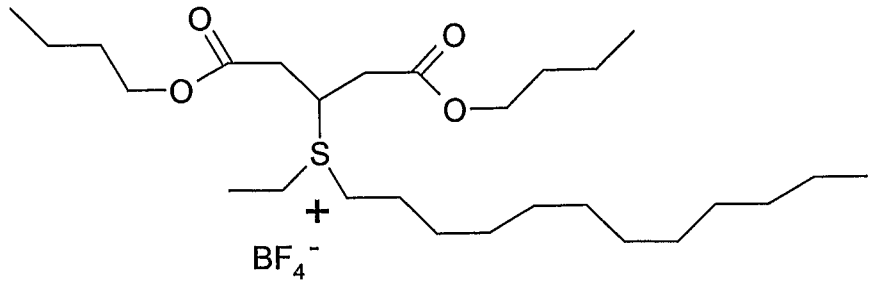
MW = 448.37 g; Eq = 448.37 g

Example 3 / Initiator - 3:



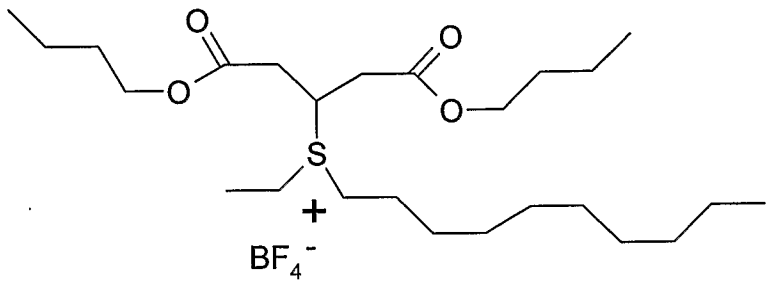
MW= 476.43 g; Eq = 476.43 g

Example 4 / Initiator - 4:



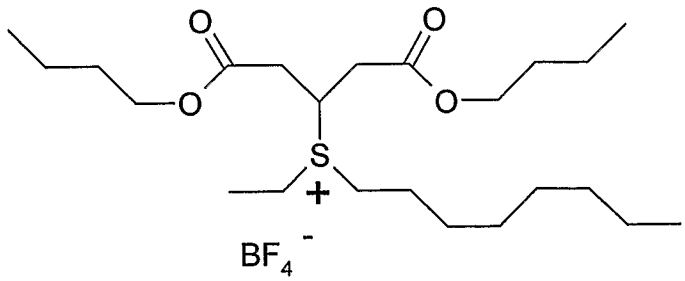
MW= 560.59 g; Eq = 560.59 g

Examples 5 / Initiator - 5:



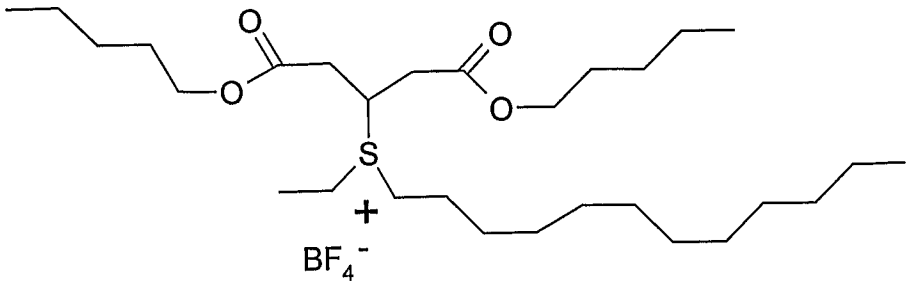
MW= 532.53 g; Eq = 532.53 g

Example 6 / Initiator - 6:



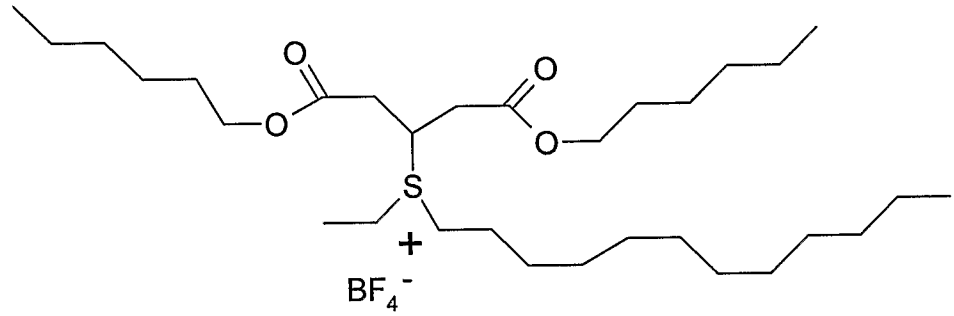
MW= 504.48 g; Eq = 504.48 g

Example 7 / Initiator - 7:



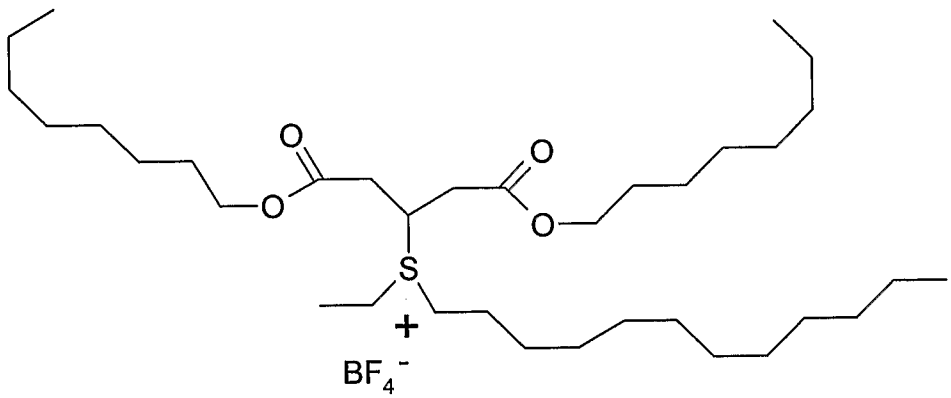
MW= 588.65 g; Eq = 588.65 g

Example 8 / Initiator - 8:



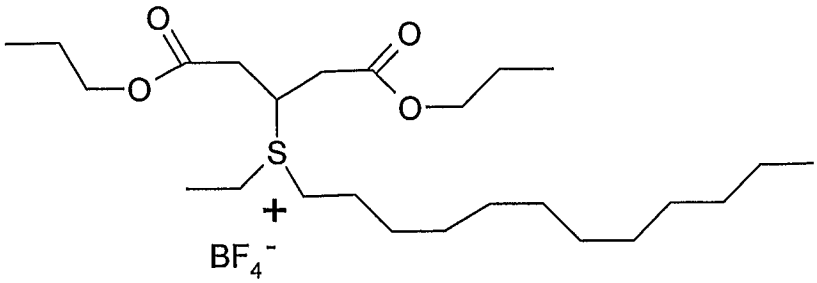
MW= 616.70 g; Eq = 616.70 g

Example 9 / Initiator - 9:



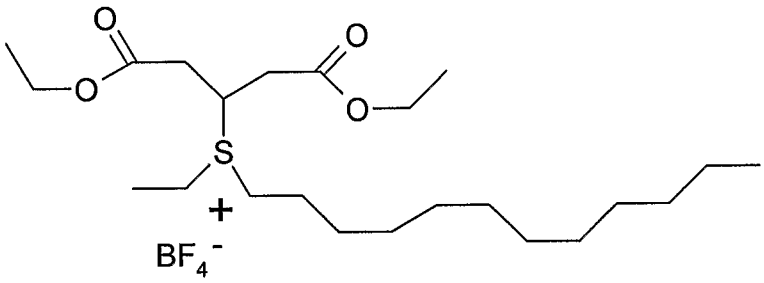
MW= 672.81 g; Eq = 672.81 g

Example 10 / Initiator - 10:



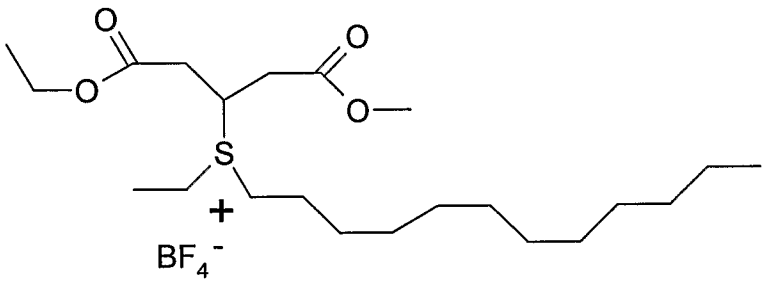
MW= 532.54 g; Eq = 532.54 g

Example 11 / Initiator -11:



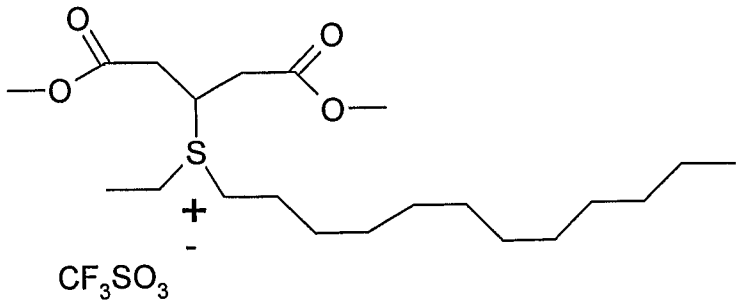
MW= 504.48 g; Eq = 504.48 g

Example 12 / Initiator - 12 :



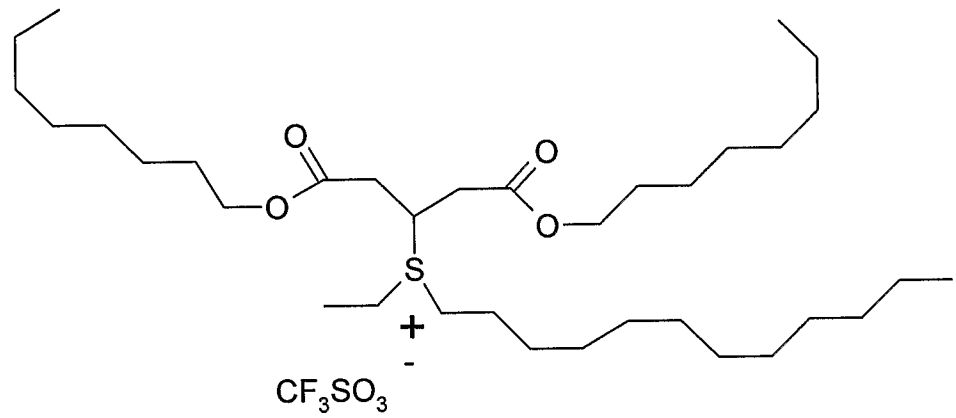
MW= 490.46 g; Eq = 490.46 g

Example 13 / Initiator - 13 :



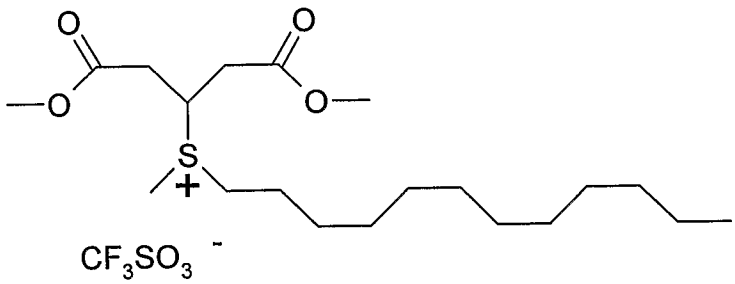
MW= 538.68 g; Eq = 538.68 g

Example 14 / Initiator - 14 :



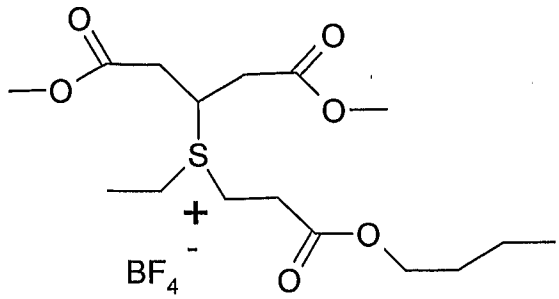
MW= 735.06 g; Eq = 735.06 g

Example 15 / Initiator - 15:



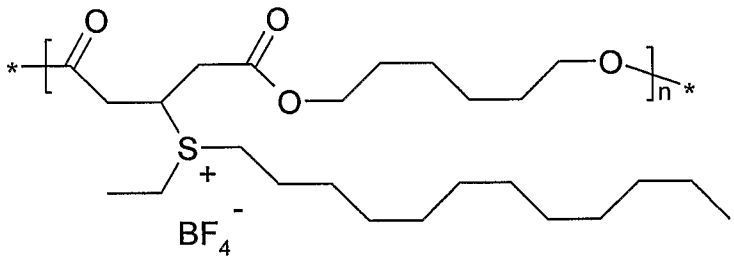
MW= 524.66 g; Eq = 524.66 g

Example 16 / Initiator - 16 :



MW= 436.27 g; Eq = 436.27 g

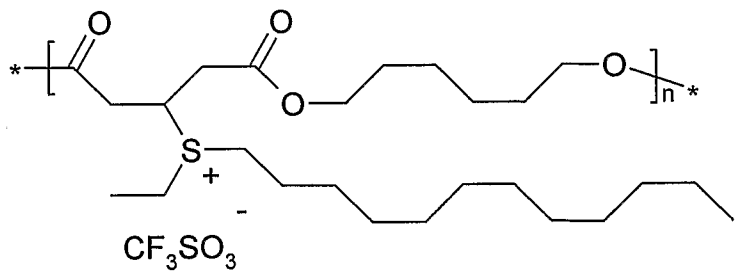
Example 17 / Initiator - 17:



(MW ≤ 20.000 g or < 10.000 g) n = 1, 2, 3, ...

Eq = 530.32 g (MW repetition unit = 530.32 g)

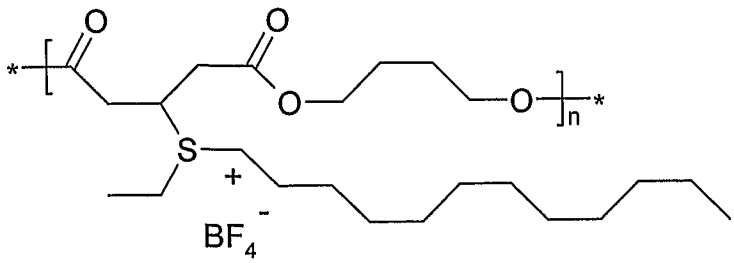
Example 18 / Initiator - 18:



(MW ≤ 20.000 g or < 10.000 g) n = 1, 2, 3, ...

Eq = 603.59 g (MW repetition unit = 603.59 g)

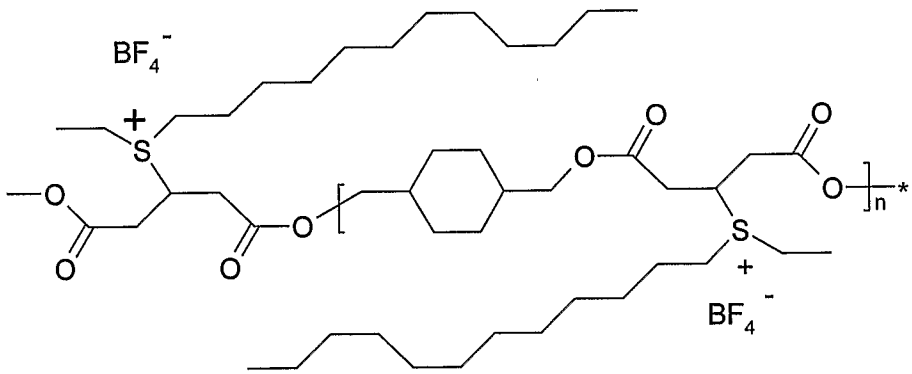
Example 19 / Initiator - 19 :



(MW ≤ 20.000 g or < 10.000 g) n = 1, 2, 3, ...

Eq = 502.46 g (MW repetition unit = 502.46 g)

Example 20 / Initiator - 20 :



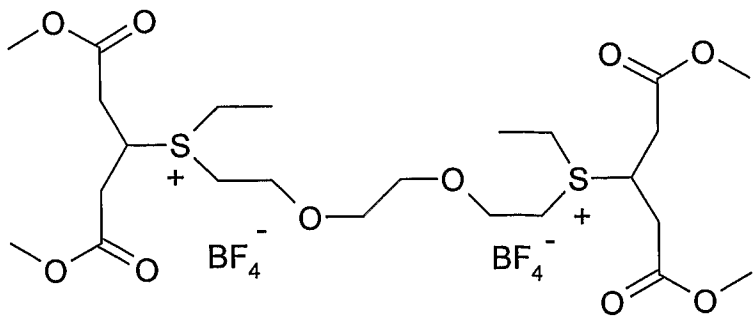
(+ Oligomers)

(n = 1, 2, 3...)

MW = about 1000 g

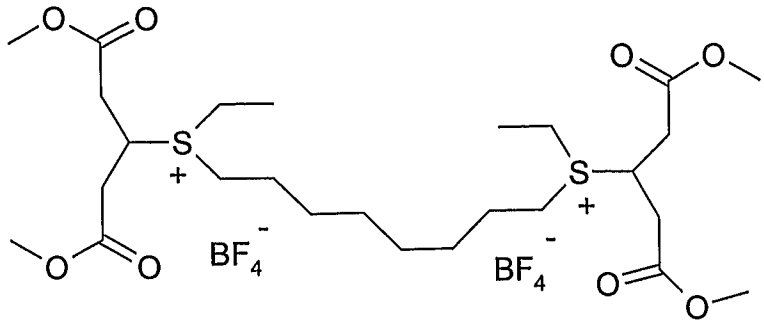
M W= 1032.98 g (contains molecules with n = 1 as main substance + Oligomers); Eq = 516.49 g

Example 21 / Initiator - 21 :



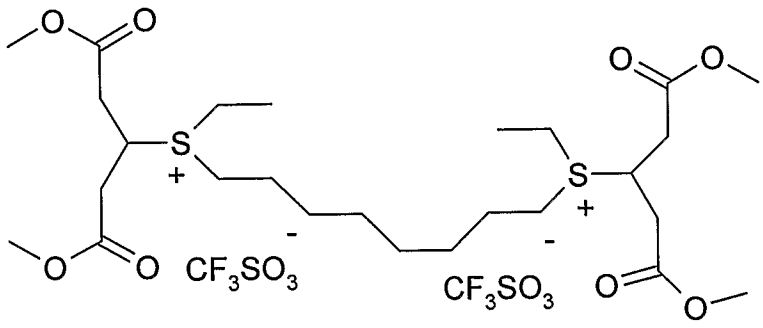
MW= 730.35 g; Eq = 365.17 g

Example 22 / Initiator - 22 :



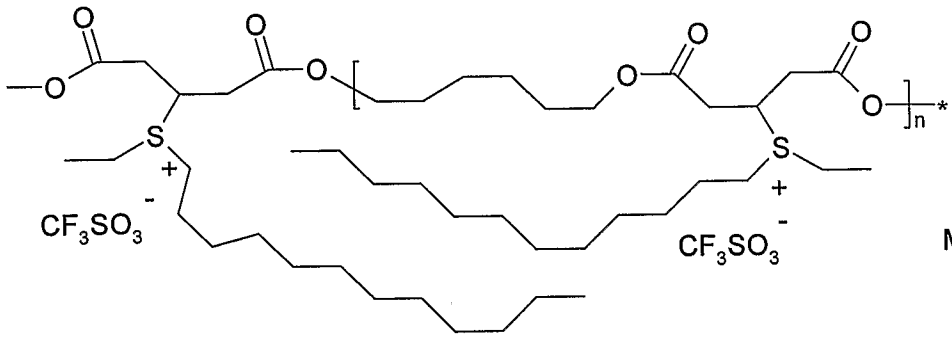
MW= 726.40 g; Eq = 363.20 g

Example 23 / Initiator - 23:



MW= 850.92 g; Eq = 425.46 g

Example 24 / Initiator - 24 :



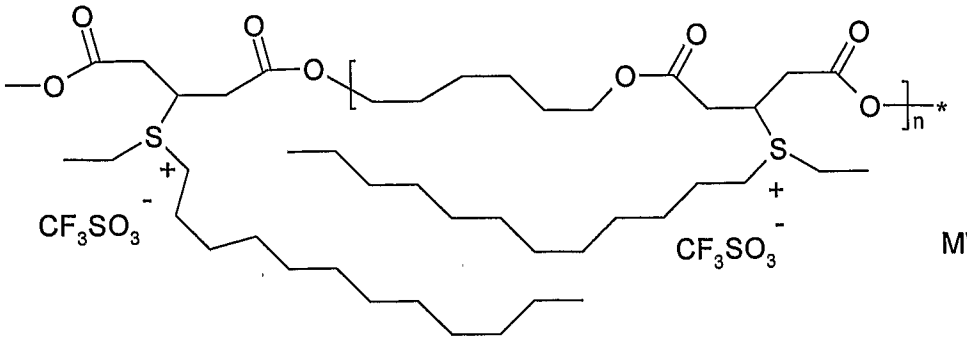
(+ Oligomers)

(n = 1,2,3...)

MW = about 1000 g

MW= 1006.94 g (contains molecules with n = 1 as main substance + Oligomers), Eq = 503.47 g

Example 25 / Initiator - 25 :



Eq = 565.73 g; MW = 1131.46 g (contains molecules with n = 1 as main substance + Oligomers)

The invention also provides a process for producing an initiator or the inventive initiator comprising the steps of

a) reacting a glutaconate, preferably a glutaconic acid ester with a thiol compound to obtain a sulfide compound,

b) optionally reacting the sulfide compound of step a) with an alcohol in a trans-esterification reaction or polycondensation reaction,

c) reacting the sulfide compound of step a) or b) with an alkylating reagent to obtain a sulfonium compound.

Another process for producing an initiator or the inventive initiator comprises the steps of

a) reacting glutaconic acid with an alcohol in an esterification reaction or polycondensation reaction to obtain a glutaconate

b) reacting the glutaconate of step a) with a thiol to obtain a sulphide compound,

c) reacting the sulphide compound of step b) with an alkylating reagent to obtain a sulfonium compound.

Thiol compounds which can be used comprise alkyl thiols and alkyl di-thiols, wherein the alkyl group is a linear, cyclic or branched $C_1 - C_{20}$ alkyl or alkylene group, wherein one or more of the methylene groups may be substituted by –CO- , -CONH-, -CON(CH_3)-, -S- and/or –O- (cf. definition of R4 in the formula I above). Representative examples of useful

thiols or di-thiols are: n-octyl thiol, n-decyl thiol, n-dodecyl thiol, HS-$(CH_2)_8$-SH and HS-CH_2CH_2-O-CH_2CH_2-O-CH_2CH_2-SH.

Alkylating reagents which can be used are reagent being able to alkylate thio ethers at the S-atom to form sulfonium coupounds. Representative examples of alkylating reagents are triethyloxonium tetrafluoroborate, ethyltriflate or methyltriflate.

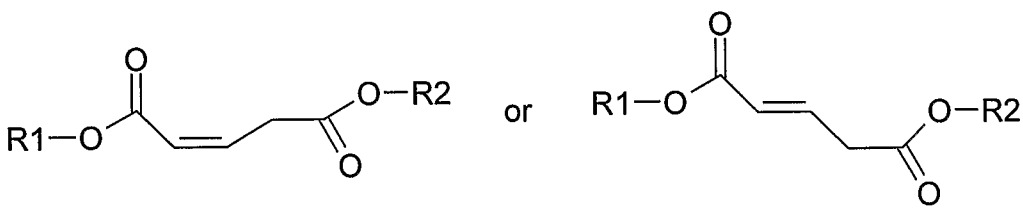
With the processes described above a variety of initiators can be produced having different viscosities but a similar reactivity towards cationically polymerizable compositions. Moreover, using the above mentioned processes, the sulfonium equivalent weight of the initiator can be adjusted to a certain range.

In a preferred embodiment, the inventive initiator can be produced using e.g. the following described procedure:

Step one: Preparation of the sulfide

Glutaconate comprising glutaconic ester according to formula B

Formula B



wherein R_1, R_2 independently from each other are a C_1 - C_{20}, preferred a C_1 - C_4 alkyl group such as methyl, ethyl, propyl or butyl

is reacted with a thiol or dithiol in the presence of a basic catalyst. Examples of useful basic catalysts include, e.g., sodium- or potassium methylate, -ethylate, -propylate or -butylate. The reaction may be performed in the presence or absence of a solvent. Examples of useful solvents include, e.g., cyclohexane, benzene or toluene. Reaction in solution is preferred but not mandatory.

The catalyst can be added to the mixture of thiol and ester, however, the mixture of ester and thiol can also be added to the catalyst. It is also possible to add the thiol and ester in parallel to the catalyst, using e.g. two dropping funnels. It is even possible to add the thiol to the catalyst (or the catalyst to the thiol) first. Afterwards, the ester is added. Typically,

addition can be done at about 20 °C to about 50 °C and it is usually completed within a few hours (e.g. about 1 to about 5 h). Applying higher temperatures may be possible, but it is not always recommended. The catalyst can be removed, for example, by washing the reaction mixture with diluted acid (such as sulfuric acid or hydrochloric acid) and then water. After removal of the solvent, the sulfide can be obtained.

Step two (optional): Transesterification or polycondensation

The sulfide obtained from step one can be mixed with about two moles of an alcohol (or about one mole of a diol), an acid or base as catalyst, and optionally a solvent.

Representative examples of useful alcohols include: 1-pentanol, 1-hexanol, 1-octanol, and cyclohexanol

Representative examples of acidic or basic catalysts include : p-toluenesulfonic acid, sulfuric acid, titanium-tetra isopropylate, potassium- and sodium tert.-butylate.

Representative examples of useful solvents include: toluene, benzene or cyclohexane.

The mixture usually is heated to about 60-150 °C for several hours (e.g., about 2 to about 10 h) or even several days (2-7 days). During the reaction, a low boiling alcohol is formed (e.g. an alcohol having a boiling point below about 120-100°C). To complete the reaction, the alcohol preferably is removed by distillation. After completion of the reaction, the catalyst can be removed, for example, by extraction with water or by treatment with Al_2O_3.(e.g. available from MP Biomedicals GmbH, 37269 Eschwege, Germany). If the reaction was carried out in a solvent, the solvent may be removed by distillation.

Step three: Reacting the sulfide obtained in step a) or b) with an alkylating reagent

After setting a flask under inert gas atmosphere such as nitrogen or argon atmosphere an excess of alkylating reagent, for example, triethyloxonium tetrafluoroborate, ethyltriflate or methyltriflate, is placed into the flask. A solvent is optionally added and the mixture is stirred to form a slurry or solution.

Representative examples of solvents that can be used are: toluene, benzene or dichloromethane.

While stirring, the sulfide obtained from step a), or optional step b), can optionally be dissolved in the same solvent (e.g., cyclohexane, benzene or toluene.) added over a

typical time frame of several hours (e.g. about 2 to about 10 h) preferably at about 10-60 °C. After addition is complete, the reaction mixture may be stirred, preferably for additional about 1-8 days, and preferably at about 10-60 °C.

A reaction without any solvent is also possible. Reaction in solution is preferred but not mandatory.

When the reaction is complete, the mixture is usually diluted with a solvent (e.g. toluene, benzene or dichloromethane) and extracted with water several times (e.g. about 2-5 times) until a pH of three or higher can be detected.

The solution is preferably dried, for example, by using sodium sulfate. After filtration, the solvent can be stripped off, e.g. using a rotary vacuum evaporator. The sulfonium compound is then obtained generally in the form of a liquid or a solid.

The inventive initiators can be used for curing a cationically polymerizable composition. Thus, the invention also provides a curable composition comprising at least one cationically polymerizable compound, preferably comprising at least two aziridine groups, as component (A) and at least one initiator as component (B). A mixture of different initiators can be used as well.

Generally, the cationically polymerizable compound is present generally in an amount of about 10-90 wt.-%, preferably in amount of about 10-80 wt.-%, and most preferably in amount of about 15-60 wt.-%, with respect to the weight of the whole composition.

Generally, the initiator is present in amount of about 1-30 wt.-%, or preferably, in amount of about 2-15 wt.-%, or most preferably, in amount of about 3-8 wt.-%, with respect to the weight of the whole composition.

Surprisingly, this class of initiators shows good curing kinetics, especially when used to cure dental impressioning materials.

Moreover, cured composition comprising the inventive initiator may also show improved linear dimensional stability (i.e., low shrinkage) compared to curable compositions known in the art cured using initators containing common sulfonium salts.

Some of the curable compositions according to the invention also have non-biting taste, and the bitter taste is either reduced or non-existing. Improved taste can have the benefit of reducing the amount of saliva formed during a dental impression process which makes

the process more pleasant for the patient and helps maintain accuracy of the dental impression.

Sometimes adjustment of the viscosity of the composition is needed, especially if compositions for different indications have to be provided. In the dental field there is often a need for formulations having different viscosities. These formulations are usually classified as light body, medium body or heavy body materials indicating an increase in viscosity.

Adjustment of the viscosity can be achieved e.g. increasing or reducing the amount of fillers or varying the molecular weight of the components of the composition. However, this can sometimes be a cumbersome undertaking as other physical properties of the composition (e.g. curing behaviour) are affected, too.

In this regard, using the inventive initiator can provide some advantages, especially in regard to dental impressioning materials. The amount of initiator used for curing these compositions can be quite high (e.g. up to about 30 % by weight). Thus, a considerable part of the so-called catalyst paste can be comprised by the initiator contributing to the viscosity of the paste.

As described above due to the presence of two carbon ester groups in the initiator, these groups can be used to connect two or more structural elements containing a sulfonium group leading to dimeric, trimeric, oligomeric or polymeric structure. By doing so, the sulfonium equivalent weight remains more or less in a certain range, independent from the molecular weight and the viscosity of the initiator, taken into account that as a general rule the viscosity of the component usually increases with its molecular weight.

Thus, the quantity (e.g. in grams) of the inventive initiator needed for initiating a curing reaction of a cationically polymerizable composition will not vary too much independent from the structure and molecular mass of the initiator due to its comparable high content of sulfonium groups represented by a certain Eq value.

This is particularly valuable in the reformulation of certain curable compositions or other compositions where it is not possible to significantly vary the ratios of the reactants, especially the ratio of base paste to catalyst paste (e.g. a ration of 5 : 1 is needed for a curable composition to be mixed in a Pentamix™ mixing device available from 3M ESPE AG).

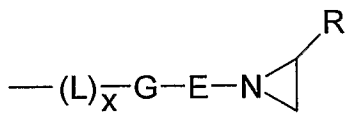
The initiators of the invention can be classified as derivatives of glutaric acid esters. In contrast to this, structural analogous mono-molecular, dimeric, oligomeric and/or

polymeric derivatives from succinic acid esters were regarded as showing a too rapid curing behaviour, whereas analogous mono-molecular, dimeric, oligomeric and/or polymeric initiators derived from 2-methylene-succinic acid esters were regarded as showing a too slow curing behaviour.

Aziridine-group-containing compounds are preferred cationically polymerizable compounds. Particularly preferred aziridine-group-containing compounds include, e.g., N-alkyl aziridine polyether containing compounds. Such compounds comprise at least two ethylene imine groups, compounds having more than two ethylene imine groups are also useful.

Such components are known and described in the art, e.g., US 3,453,242, US 5,569,691, and US 6,383,279 B1. These documents, especially as regards their disclosure about aziridine-group-containing compounds is explicitly mentioned and herewith incorporated by reference.

Preferably, the aziridine groups are attached to an oligomeric and/or polymeric hydrocarbon, ester, ether or siloxane backbone. Such attached aziridine groups can be represented by the formula



wherein

R represents H, C_1-C_{12} alkyl, C_2-C_{12} alkenyl, C_2-C_{12} alkinyl, C_7-C_{15} alkylaryl, C_7-C_{15} arylalkyl or C_3-C_{12} cycloalkyl, and wherein hydrogen atoms can be replaced by Cl or F and/or wherein up to about 5 carbon atoms may be replaced by atoms or group of atoms selected from O, CO, N or S,

E represents a C_1 – C_{18} branched or unbranched hydrocarbon chain wherein up to about 5 carbon atoms can be replaced by atoms or group of atoms selected from O, CO, N or S,

G represents a group selected from C(O)O, C(O)NR, C(O) or C(O)C(O), $C(O)(CH_2)_mC(O)$, with m = 1 to 10, C(S)NR or CH_2,

L represents O, S or NR, with x = 0 or 1.

If used as a dental impression material, the cationically polymerizable compound can be present in an amount in the range of about 35-90 % by weight, or preferably about 40-75 % by weight with respect to the weight of the cured composition.

If used as a dental duplicating material, the cationically polymerizable compound can be present in an amount in the range of about 10-25 % by weight, or preferably about 12-20 % by weight with respect to the weight of the cured composition.

The molecular weight (M_n) of the cationically polymerizable compound before curing is typically in the range of about 600-20,000 g/mol, and preferably about 1,000-10,0000 g/mol, as determined by GPC using appropriate techniques known in the art.

A useful method for determination of the molecular weight of organic polyols is a GPC method using a combination of PSS SDV 10.000 Å + PSS SDV 500 Å with column dimensions 8x300 mm and a particle size of 5 µm. In addition, a pre-column PSS SDV 100 Å with column dimensions 8x50 mm and a particle size of 10 µm is used. The eluent is THF stabilized with Jonol running with a flow rate of 1,0 ml/min. The detector is a refractive index detector (RI), the injection volume 100 µl. The samples have a concentration of 1 % (solvent THF). Polystyrol standards are used.

In addition, the curable composition of the invention may comprise filler(s) as optional component (C) and also additive(s) as optional component (D).

A wide variety of inorganic, especially hydrophobic fillers may be employed such as silicas, aluminas, magnesias, titanias, inorganic salts, metallic oxides and glasses. It is also possible to employ mixtures of silicone dioxides, including those derived from crystalline silicone dioxide, such as pulverized quartz (4 to 6 µm); amorphous silicone dioxides, such as a diatomaceous earth (4 to 7 µm); and silanated fumed silica, such as Cab-o-Sil TS-530 (160-240 m^2/g), manufactured by Cabot Corporation. Varying the sizes and surface areas of the foregoing materials enables one to control the viscosity and thixotropicity of the uncured compositions as well as the physical properties of the cured compositions. Some or all of the foregoing hydrophobic fillers may be surface treated with one or more silanating agents, such as known to those of ordinary skill in the art. Such silanating may be accomplished, e.g., using known halogenated silanes or silazides. Some useful functionalized silicas are commercially available, e.g. products sold under the brands Aerosil™ (Degussa) or HDKH™ (Wacker).

Among the fillers which can be used are non-reinforcing fillers such as quartz, cristobalite, calcium silicate, diatomaceous earth, zirconium silicate, montmorillonite such as bentonite, zeolite, including molecular sieves such as sodium aluminium silicate, metal oxide powder such as aluminium or zinc oxide or their mixed oxides, barium sulphate, calcium carbonate, plaster, glass and plastic powder. The non-reinforcing fillers can be surface treated. The surface treatment can generally be carried out with the same methods as described for the reinforcing fillers.

Suitable fillers also include reinforcing fillers such as e.g. pyrogenic or precipitated silicic acid and silica aluminium mixed oxides. The above mentioned fillers can be hydrophobized, e.g. by treatment with organosilanes or siloxanes or by the etherification of hydroxyl groups to alkoxy groups. One type of filler or also a mixture of at least two fillers can be used. The particle distribution is preferably chosen such that there are no fillers with particle sizes of more than 50 µm.

A combination of reinforcing and non-reinforcing fillers can be desirable. In this respect, the quantity of reinforcing fillers in the composition may range from about 0.1-15 wt.-%, and in particular, from about 1-10 wt.-%. The difference in the named overall ranges, i.e. about 9 to about 80 wt.-%, can be accounted for by non-reinforcing fillers.

Because the filler is an optional component, it may not be present at all, but typically it will be present in the curable composition at an amount of from about 0-80 wt.-%, preferably about 5-70 wt.-%, or more preferably about 10-60 wt.-% based upon the weight of the total composition.

Besides filler(s), additives can be present like dyes, pigments, thixotropic agents, flow improvers, polymeric thickeners, surfactants, odorous substances, diluting agents and/or flavourings. All kinds of known and compatible softeners and rheology modifiers like non-reactive polymeric fluids or fats commonly used in commercialized impression materials can be added as well as pigments and stabilizers of any kind.

Preferred are those ingredients and additives that do not add unpleasant smell or taste. Compounds that have an unpleasant smell might be removed by thinfilm evaporation, if needed.

Examples of suitable thixotropic agent(s) that can be added to the curable composition of the invention include organic compounds, e.g., waxes according to the definition in Ullmanns Enzyklopädie der technischen Chemie, 4. Auflage, Verlag Chemie, Weinheim,

Band 24, page 3, or triglycerides (as described in US 6,127,449). In general, all organic, non-aqueous thixotropic agents can be suitable.

Some of the untreated or surface treated inorganic fillers mentioned above may also contribute to the rheological properties of the formulation. Fillers that contribute to the thixotropic rheological properties of the curable compositions may be selected from the group of inorganic fillers are modified or unmodified bentonite(s), kaoline(s) and the like.

Representative examples of surfactant(s) include, e.g., polyethers and polyether-type materials Such surfactants include, for example, those sold under the trademarks Pluronic™, Synperonic™, Silwet™ type materials. Especially useful are substances described in US 5,569,691 A1 the disclosure of which (especially in regard to surfactants) is herewith incorporated by reference.

Generally, suitable diluting agent(s) are liquids. Preferred diluting agents do not contain moieties: -SH, –COOH, or primary or secondary amino groups, but they may contain –OH groups. Liquids such as C_{12}-C_{15} alkyl acetates, liquid derivatives of citric acid, esters of phthalic acid with branched alcohols like bis(2-ethylhexyl)phthalate or polymeric phthalates, C_2-C_{18} bis(alkyl)esters of C_2-C_6 dicarboxylic acids like dioctylmaleate, dioctyladipate, aromatic and aliphatic esters of sulfonic acids (like those sold under the trademark Mesamoll™), aromatic and aliphatic amides of sulfonic acids like N-ethyl toluene sulfonic acid amide or N-butyl benzene sulfonic acid amide. Typical aromatic diluters like polyphenyls, dibenzyl toluene, xylyl toluene, dixylyl toluene and polymeric compounds like polyethers, polyesters, polycarbonates, polyolefins also can be used. Also, low molecular weight alcohols that contain more than one OH-functionality, like propane-1,2, diol, may be used. From the group of polymeric compounds, polypropylene glycols and its derivatives are preferred.

Generally, the additive(s) can be present in amount of about 0-89 wt.-%, or preferably in amount of about 5-85 wt.-%, or most preferably in amount of about 10- 80 wt.-% with respect to the weight of the cured composition.

If used as a dental impression material the additive(s) are typically used in an amount in the range of about 10-65 %, or preferably in the range of about 25-60 % with respect to the weight of the cured composition.

If used as a dental duplicating material the additive(s) typically can be present in the range of about 10- 90 weight %, or preferably in the range of about 20-85 % by weight with respect to the cured composition.

Thus, typical compositions for the curable composition of the invention comprise components (A) to (D) in the following amounts:

Component (A): about 10 % to about 90 wt.-%

Component (B): about 1 wt.-% to about 15 wt.-%

Component (C): about 0 wt.-% to about 80 wt.-%

Component (D): about 0 wt.-% to about 89 wt.-%.

The curable composition, after curing, preferably satisfies at least one, and preferably two or moreof the following characteristics:

- Shore A hardness (DIN 53505, measured 24 hours after mixing) above about 10, or preferably above about 15. Values up to about 80, up to about 75 or up to about 70 can be reached.
- Tensile strength (MPa) above about 0,2, or above about 0,3, or above about 0,4. Values up to about 6, up to about 5 or up to about 4 can be reached.
- Elongation at break (%) above about 30, or above about 50, and or above about 80. Values up to about 300, up to about 250 or up to about 200 can be reached.

  Tensile strength and Elongation at break are measured according to Deutsche Industrie Norm (DIN) or European Norm (EN) Method # 53504 (geometry S2, 200 mm/min) using Universalprüfmaschine Zwick Z020 (Zwick GmbH &Co, Ulm, Germany).
- For precision impression materials the values for linear dimensional change (ISO 4823: 2000) are within the limits according to ISO 4823:2000.
- Consistency and recovery after deformation are within the limits of ISO 4823:2000. The curable compositions can be formulated to provide materials of various viscosities, from light body-type materials (Type 3) to putty materials (Type 0) according to ISO 4823:2000.

The invention also relates to a process for producing a curable composition comprising the steps of

- providing component (A) comprising a cationically curable compound as described above and component (B) comprising the inventive initiator as described above,
- mixing component (A) and component (B).

The other optional ingredients like filler(s) and additive(s) can be present either in component (A) or component (B) or in both components (A) and (B).

The typical volumetric mixing ratios of component (A) and component (B) for dental materials are in the range of about 0.5 : 1 to about 15 : 1, or preferably, in the range of about 1 : 1 to about 10 : 1. Especially preferred is a volumetric mixing ratio of about 5 to about 1.

Dosing of the components can be carried out by sight (strand-length comparison), by weight, via pre-dosed pack units and subsequent manual mixing, from double-chambered cartridges with static mixing tubes or by means of volume dosing systems with downstream static or dynamic mixers.

An especially useful device for mixing the components for dental applications is the device described in US 5,286,105 and available on the market as the Pentamix™ machine or Pentamix™ 2 machine (from 3M ESPE AG). Mixing, however, can also be performed manually.

Often formulations are provided as two or multi-part system (such as a kit), in which two or more parts of the composition are stored separately and combined, e.g., by mixing, upon use.

According to the invention, the first part (i.e., part I or base paste) of a typical two-part system comprises the cationically curable compound and the second part (i.e., part II or catalyst paste) comprises the initiator. Both parts are stored separately from each other until they are mixed prior to use.

The invention also provides a use of the inventive initiators as described herein for initiating the cure of a cationically polymerizable substance (e.g., the cationically polymerizable compound).

The curable composition as described above can be used broadly for coating substrates, as sealing materials, moulding materials, for adhesively fixing substrates, making impressions, and/or for the modeling of objects or body parts.

The curable composition is especially useful for producing dental materials like precision impression materials, bite registration materials, duplicating materials, modeling materials, situation impression materials.

In this respect, the composition can be used e.g. for making impressions of soft and hard dental tissue. This can be achieved simply, e.g. filling the material into a dental tray and putting the tray into the mouth of a patient.

If used in the dental field, curing is preferably carried out at a temperature below about 50 °C and preferably below about 40 °C, and more preferably below about 30 °C. A typical time for cure of curable compositions of the invention used for dental impressioning is within about 20 min, or preferably within about 10 min, after mixing the components of the composition. For dental duplicating applications or dental modelling applications that take place in the professional dental laboratory, cure times of up to 45 min is generally acceptable . In other applications(e.g., sealing, moulding, coating, adhesively fixing), other cure times may be typical and higher cure temperatures may be acceptable. Nevertheless, setting times in the range of about 30 min or about 1 hour can still be useful.

The material is generally regarded as cured if the cured material fulfils the requirements for its use. For example, a dental precision impression material typically fulfils the requirements for its use when it fulfils the requirements of ISO 4823:2000 (such as compatibility with gypsum, strain in compression, recovery from deformation, detail reproduction, linear dimensional change).

Especially in the dental field two further parameters might be of some importance: working time and oral setting time.

According to DIN EN ISO 4823:2000 impression materials can be classified as Type 0 (kneadable), Type 1 (high viscosity), Type 2 (medium viscosity), and Type 3 (low viscosity).

The total working time at room temperature (23 °C) measured according to DIN EN ISO 4823:2000 for Impregum™ Garant L DuoSoft and Permadyne™ Garant L 2:1 (3M ESPE AG), both Type 3 regular setting polyether precision impression materials, is 3 min 40 s ± 15 s and 4 min ± 15 s, respectively.

The oral setting time is given by the manufacturer in the instructions for use. According to DIN EN ISO 4823:2000 the elastomeric property recovery from deformation of the vulcanized material have to reach values of ≥ 96.5 % within the recommended oral setting time. In addition according to DIN EN ISO 4823:2000 the elastomeric property strain in compression of the vulcanized material has to come up to a value within the range of 0.8 to 20.0 % for Type 0 and Type 1 materials and in the range of 2.0 to 20.0 % for Type 2 and Type 3 materials, respectively within the recommended oral setting time.

If the composition is to be used as dental impression material, appropriate working times are in a range of about 20 s to about 7 min or about 30 s to about 6 min at room temperature (23 °C). For impression materials oral setting times should be as short as possible. Suitable oral setting times are ≤ about 6 min or ≤ about 5 min.

If used in the dental field, the composition can be applied using e.g. the following steps:

- providing the components of the composition,
- mixing the components,
- applying the composition to a surface,
- letting the composition set.

The surface can be the surface of soft or hard oral tissue, the surface of an impression material, preferably of a cured impression material, the surface of a crown or the surface of a model of a tooth stump.

EXAMPLES

The invention is hereinafter described by examples. The examples are not intended to limit the scope of the invention.

Test Methods

Tensile strength (MPa) and Elongation at break (%)

Tensile strength and Elongation at break were measured according to Deutsche Industrie Norm (DIN) or European Norm (EN) Method # 53504 (geometry S2, 200 mm/min) using Universalprüfmaschine Zwick Z020 (Zwick GmbH &Co, Ulm, Germany).

Shore A hardness (after 24 hours)

Shore A hardness was measured according to Deutsche Industrie Norm (DIN) Method # 53505. The curable compositions were allowed to cure for 24 hours at 23°C and ambient humidity before the hardness was measured.

Recovery after deformation, Linear dimensional change (shrinkage), Consistency

were measured according to EN ISO 4823:2000.

Citric acid esters employed in catalyst paste:

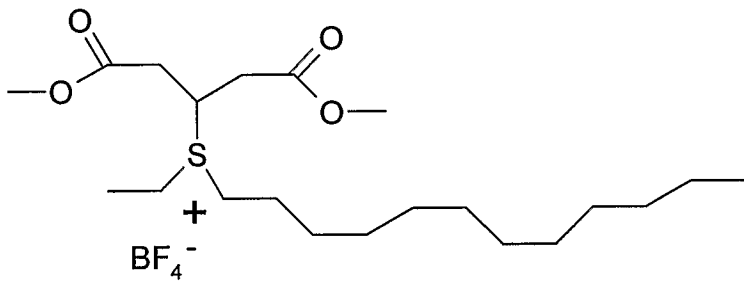
A acetyl tri-n-butyl citrate (CAS 77-90-7)
B acetyl tri-n-hexyl citrate (CAS 24817-92-3)
C acetyl tri-2-ethylhexyl citrate (CAS 144-15-0)

Initiators employed:

See formulas for initiators 1 to 25 above.

Process for producing individual Initiator Compounds

Production Example 1 (Initiator – 3)

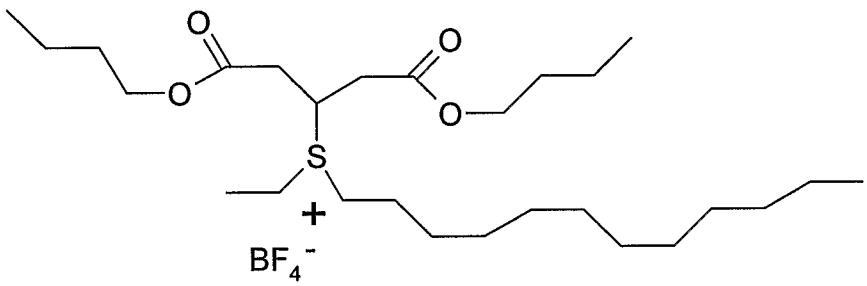


Step a): Under nitrogen atmosphere, 150 g cyclohexane and 2.25 g of a 30 % solution of sodium methylate in methanol were placed in a four-necked round bottom flask. The mixture was stirred. Then 37.7 g dodecylthiol and 30.0 g dimethylglutaconate were added parallel via two dropping funnels within one hour. The reaction exothermed to 35 °C. Stirring was continued for one more hour, after which an NMR spectrum showed that the reaction was complete. The mixture was diluted with 200 ml cyclohexane. It was then extracted twice with 250 ml 2N sulphuric acid and twice with 250 ml of water. The last

extract showed a pH of 7. The solution was separated and filtered. After removing cyclohexane with a rotary evaporator, a slightly yellow liquid was obtained in 92 % yield (61.9 g).

Step c): In a three-necked round bottom flask, 32.9 g triethyloxonium tetrafluoroborate and 50.0 g toluene were placed under nitrogen atmosphere. Under stirring at room temperature 50.0 g sulfide (from step a)) was added within six hours. The mixture was stirred vigorously for additional three days. A ^{1}H-NMR spectrum showed that the reaction was complete. The mixture was diluted with 50 ml toluene. It was extracted six times with 200 ml water. The last water extract showed a pH of 3. 12.5 g of anhydrous sodium sulphate were added. After filtration and removing the solvent, a yellow liquid was obtained in 93 % yield (61.3 g).

Production Example 2 (Initiator – 4)



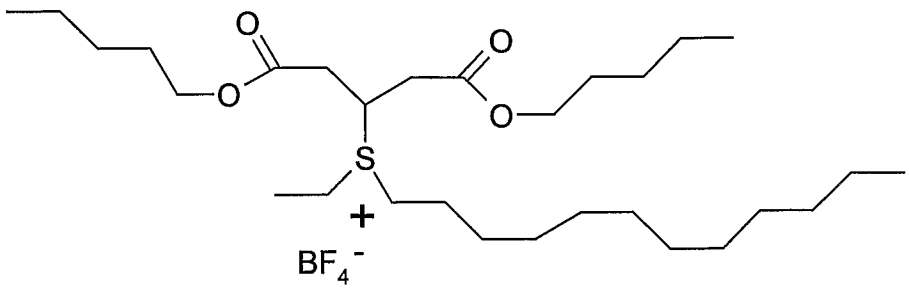
Step a): See above (step a) of Production Example 1)

Step b): 9.65 g of sulfide (from step a)), 20 ml of 1-butanol and 200 mg p-toluene sulfonic acid monohydrate were placed in a round bottom flask. The solution was heated to 100°C under nitrogen atmosphere for 24 hours. Then about 10 ml of butanol/methanol mixture were distilled off. 15 ml butanol were added and the solution was again heated to 100°C for 24 hours. A ^{1}H-NMR-spectrum showed that the reaction was nearly complete. The solvent was removed completely in a high vacuum rotary evaporator. 40 ml cyclohexane and 8.3 g basic alumina were added. After shaking the slurry for 10 minutes and filtration, the solvent was removed again. 11.2 g of a clear, nearly colourless liquid were obtained (82 % yield).

Step c): 21.4 g triethyloxonium tetrafluoroborate were put into a three-necked round bottom flask under nitrogen atmosphere. 45 ml toluene were added and the mixture was stirred. To the slurry, 40.0 g sulfide was added within two hours under stirring. Stirring was continued for additional four days at which time the reaction was nearly complete. 50

ml toluene were added and the solution was extracted six times with 80 ml water. The last extract showed a pH of 3. The solution was dried with 6 g anhydrous sodium sulfate and filtered. After removing the solvent 46.2 g (92 %) of a yellow brownish liquid were obtained.

Production Example 3 (Initiator -7)



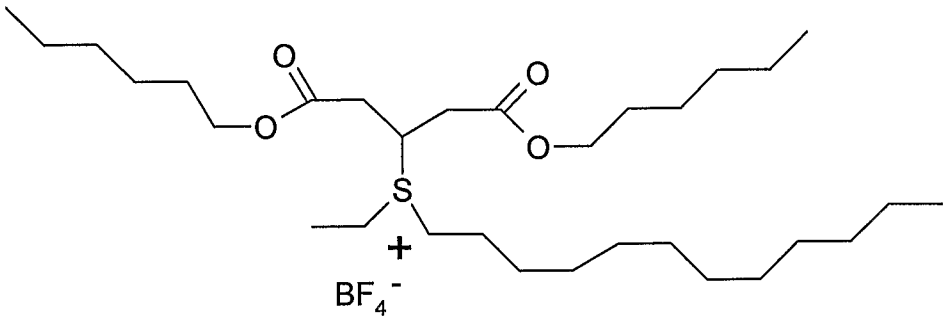
Step a): 2.22 g of a 30 % solution of sodium methylate in methanol were filled into a three-necked round bottom flask. Under nitrogen atmosphere, 150 g cyclohexane was added. 30.0 g dimethylglutaconate and 36.5 g dodecylthiol were added parallel via two dropping funnels under stirring within one hour. During the addition, the temperature of the mixture rose to 30 °C. After 30 minutes, a ^{1}H-NMR-spectrum showed that the reaction was complete. The solution was diluted with 200 ml cyclohexane. It was extracted two times with portions of 200 ml 2 N sulphuric acid and two times with portions of 200 ml water. The last extract showed a pH of 7. After separation, the organic layer was filtered and the solvent was removed. A slightly yellow liquid was obtained in 93 % yield (60.1 g).

Step b): 34.2 g sulfide (from step a)), 20.9 g 1-pentanol, 1,1 g p-toluene sulfonic acid monohydrate and 55.1 g toluene were filled into a three-necked round bottom flask. The solution was heated to reflux (111°C) under nitrogen atmosphere and stirring. After thirty hours, the reaction was complete. Basic alumina (30.0 g) was added at room temperature. The slurry was stirred for one hour. After that the mixture was filtered. After removing the solvent, 43.2 g (96 %) of a clear, slightly yellow liquid were obtained.

Step c): 20.83 g triethyloxonium tetrafluoroborate were filled into a three-necked round bottom flask. Under nitrogen atmosphere 43.2 g toluene were added. 43.2 g sulfide (from step b)) was added via dropping funnel under stirring at room temperature within 1.5 hours. After stirring for one week, the reaction was nearly complete. The solution was diluted with 40 ml toluene and extracted 6 times with 50 ml portions of water. The last extract showed a pH of 3. The organic layer was dried with sodium sulphate and filtrated.

The solvent was removed in a vacuum rotary evaporator. 51.4 g (96 %) of a clear, orange liquid were obtained.

Production Example 4 (Initiator -8)



Step a): See step a) of Production Example 3

Step b): 50.0 g sulfide of step a), 35.9 g 1-hexanol and 850 mg p-toluene sulfonic acid monohydrate were filled into a three necked round bottom flask with stirrer and nitrogen inlet. The mixture was set under nitrogen atmosphere and heated to 100 °C for 1 week. The formed methanol was distilled off three times during the reaction. After one week a ^{1}H-NMR-spectrum showed more than 96 mole percent hexylester. The mixture was diluted with 50 ml toluene and 40 g of basic alumina were added. After stirring for one hour, the slurry was filtered. The solvent was distilled off in a high vacuum rotary evaporator. 53.2 g of a yellow liquid were obtained (77 % yield).

Step c): In a three-necked round bottom flask 25.2 g triethyloxonium tetrafluoroborate and 70 ml toluene were placed under nitrogen atmosphere. Under stirring at room temperature 53.2 g sulfide (of step b)) were added within five minutes. The mixture was stirred vigorously. After seven days the reaction was complete. The mixture was transferred into a separating funnel under addition of 50 ml toluene. It was extracted six times with 100 ml portions of water. The last water extract showed a pH of 3. After separation the solution was dried with 15 g anhydrous sodium sulphate. After filtration and removing the solvent a clear, yellow liquid was obtained. Yield was 60.1 g (92 %).

Production of the other initiators used in Composition Examples 1 to 16 in Table 1 below can be accomplished in a similar way.

Composition Examples 1-16

Composition Examples 1-16 describe impression materials with a medium bodied consistency employing the sulfonium compounds described in Examples 1 - XX as initiators of cationic ring-opening polymerization.

Catalyst Paste: Initiator was employed in the amount of 5.008 10^{-2} mole per 100 g catalyst paste (19,30 % to 46,40 % by weight). The combined amount of initiator and citric acid ester was always 59.80 % by weight. This resulted in 13.40 % by weight to 40.50 % by weight for citric acid ester. Thus, the higher the molecular weight of the initiator, the lower the amount of citric acid ester. Other components of the catalyst paste (comprising a total of 31.20 % by weight) were: 3.50 % by weight surfactant (copolymer EO (ethylene oxide) /PO (propylene oxide)), 24.10 % by weight highly dispersed surface traeted silica (HDKHTM (Wacker).), 12.10 % by weight diatomaceous earth and 0.50 % by weight pigments. Citric acid ester was used to first dissolve the initiator. Then the remaining components were added and mixed.

Base paste: 53.50 % by weight difunctional aziridino polyether (EO (ethylene oxide) / THF (tetrahydrofuran) polyether back bone; M_n 6000) with a low content of cyclic polyether compounds as described in US 6, 383 279 A1, 15.10 % by weight fat (trisacylic ester of glycerine), 7.76 % by weight dibenzyl toluene, 14.70 % by weight polymeric polyether softener (EO (ethylene oxide) / THF (tetrahydrofuran) polyether backbone; M_n 6000), 6.50 % by weight diatomeceous earth, 0.54 imidazole compound and 1.90 weight % pigments, flavourings and fragrances.

The dental impression material was prepared by mixing 1.00 g of base paste with 0.24 g of catalyst paste using a spatula. The resulting mass was allowed to cure at room temperature for 24 hours before the Shore A hardness was measured.

A summary showing the initiator used and the type of citric acid ester employed, as well as the Shore A hardness of the resulting medium-bodied impression material is presented in Table 1. The characterization of the initiators as I – 1 to I – 25 in Table 1corresponds to the characterization of the initiators listed above.

Comparative Example 1

Initiator Example 41 in US 4,167,618

Table 1

Example	Initiator	Citric acid ester used in cat. paste	Shore A hardness
1	I – 1	B	46
2	I – 2	B	45
3	I – 3	A	46
4	I – 3	B	45
5	I – 4	B	45
6	I – 5	B	45
7	I – 6	B	47
8	I – 7	B	45
9	I – 8	B	46
10	I – 9	B	46
11	I – 9	C	45
12	I – 10	B	47
13	I – 11	B	46
14	I – 16	B	47
15	I – 18	A	43
16	I – 25	A	44
Comp. Ex 1	Current	A	46

Composition Examples 17-26

Sulfonium compounds were compounded into catalysts pastes as above and mixed with base pastes to form dental impression materials. In Examples 17-26, the impression materials were also medium-bodied consistency as in Examples 1-16. The systems differ, however, in the Examples 17-26, wherein a higher amount of difunctional aziridino polyether was used.

The catalyst pastes were the same as employed for Examples 1-16.

The base paste for Examples 17-26 comprised: 58.00 % difunctional aziridino polyether (EO (ethylene oxide)/THF (tetrahydrofuran) polyether back bone; Mn 6000) with a low content of cyclic polyether compounds as described in US 6, 383 279 A1, 13.60 % fat (trisacylic ester of glycerine), 0.88 % surfactant (copolymer EO (ethylene oxide) /PO

(propylene oxide)), 11.60 % dibenzyl toluene, 13.90 % diatomaceous earth, 0.65 imidazole compound and 1.37 % pigments, flavourings and fragrances.

1.00 g of base paste was mixed with 0.24 g catalyst paste using a spatula. The resulting impression material was allowed to cure at room temperature for 24 hours before measurements were made according to the methods described above under TEST METHODS.

Comparative Example 2

Initiator Example 41 in US 4,167,618

Table 2

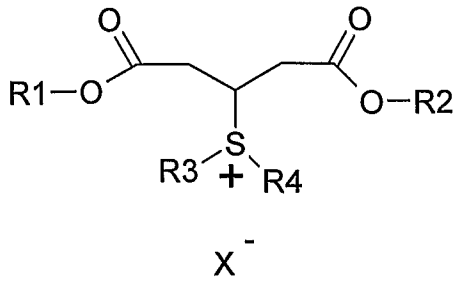
Example	Initiator	Citric acid ester type (cat. Paste)	Shrinkage (%)	Consistency (mm)	Recovery (%)	Tensile Strength (MPa)	Elongation at break (%)
17	I - 3	B	- 0.24	35.5	98.20	2.32± 0.17	258 ± 38
18	I - 4	B	- 0.20	36.0	98.34	2.47± 0.12	258 ± 21
19	I - 5	B	- 0.19	36.0	98.12	2.52± 0.13	291 ± 29
20	I - 7	B	- 0.17	35.5	98.17	2.42± 0.15	272 ± 33
21	I - 8	B	- 0.19	35.5	98.10	2.36± 0.10	259 ± 21
22	I - 17	A	- 0.13	n.d.	n.d.	n.d.	n.d.
23	I - 20	A	- 0.22	n.d.	n.d.	n.d.	n.d.
24	I - 23	A	- 0.22	n.d.	n.d.	n.d.	n.d.
25	I - 24	A	- 0.08	n.d.	n.d.	n.d.	n.d.
26	I - 25	A	- 0.14	n.d.	n.d.	n.d.	n.d.
Comp. Example	Current	A	- 0.44	36.5	98.40	2.46±	272 ± 27

2	0.11

n.d. = not determined

Claims

1. Initiator comprising at least one structural element characterized by the following formula:



wherein

X^- is a non or low coordinating anion,

R1, R2, R3, R4 are independently linear, cyclic or branched C_1 – C_{20} alkyl or alkylene groups, wherein one or more of the methylene groups contained in the alkyl or alkylene group can be substituted by –CO-, -CONH-, -CON(CH_3)-, -S- and/or –O-,

and wherein R1, R2, R3 and/or R4 can act as a bridging element connecting two or more structural elements.

2. Initiator according to claim 1 having a molecular weight in the range of about 250 to about 25,000 g/mol, wherein the molecular weight is expressed by MW for monomers and Mn (number average molecular weight) for oligomers and/or polymers.

3. Initiator according to any of the preceding claims with a sulfonium equivalent weight Eq in the range of about 300 to about 800 g/mol, wherein Eq is determined as molecular mass of the initiator divided by number of sulfonium groups present in the initiator.

4. Initiator according to any of the preceding claims, wherein X^- is selected from the group consisting of BF_4^-, $CF_3SO_3^-$, SbF_6^-, AsF_6^- or 2,5-di-chloro-benzolsulfonate.

5. Initiator according to any of the preceding claims, wherein

R1, R2 independently from each other is methyl, ethyl, n-propyl, 2-propyl, n-butyl, sec-butyl, tert.-butyl, n-pentyl, n-hexyl, n-heptyl or n-octyl and wherein one or more methylene groups of R1 and R2 can be substituted by –CO- , -CONH-, -$CON(CH_3)$-, -S- and/or –O-,

R3 is methyl, ethyl, n-propyl, 2-propyl, n-butyl, sec-butyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl or n-octyl,

R4 is R3, n-nonyl, n-decyl, n-undecyl or n-dodecyl and wherein one ore more of the methylene groups of this alkyl chain can be substituted by –CO- , -CONH-, -$CON(CH_3)$-, -S-and/or –O-.

6. Process for producing an initiator comprising the steps of

a) reacting a glutaconate with a thiol compound to obtain a sulphide compound,

b) optionally reacting the sulphide compound of step a) with an alcohol in a transesterification reaction or polycondensation reaction,

c) reacting the sulphide compound of step a) or b) with an alkylating reagent to obtain a sulfonium compound.

7. Process for producing an initiator comprising the steps of

a) reacting glutaconic acid with an alcohol in an esterification reaction or polycondensation reaction,

b) reacting the glutaconate of step a) with a thiol to obtain a sulphide compound,

c) reacting the sulphide compound of step b) with an alkylating reagent to obtain a sulfonium compound.

8. Curable composition comprising

(A) at least one cationic polymerizable compound as component (A),

(B) at least one initiator as described in any of claims 1 to 4 as component (B),

(C) optionally filler as component (C),

(D) optionally other additives as component (D).

9. Curable composition according to claim 8, wherein the cationic polymerizable compound contains aziridine groups.

10. Curable composition according to claim 8 or 9, wherein components (A) to (D) are contained in the following amounts:

Component (A): about 10 wt.-% to about 90 wt.-%

Component (B): about 1 wt.-% to about 30 wt.-%

Component (C): about 0 wt.-% to about 80 wt.-%

Component (D): about 0 wt.-% to about 89 wt.-%.

11. Curable composition according to any of claims 8 to 10 having at least one of the following properties:

- Shore A hardness (DIN 53505, measured 24 h after mixing) above about 40 to 80;
- Tensile strength according to DIN EN 53504 (MPa) above about 0,4;
- Elongation at break according to DIN EN 53504 (%) above about 50.

12. Kit of parts comprising

Part I comprising component (A), optionally component (C) and/or component (D) and

Part II comprising component (B), optionally component (C) and/or component (D)

wherein components (A) to (D) are defined as described in any of claims 8 to 11 above.

13. Process of producing a curable composition as described in any of claims 8 to 11 comprising the steps of

providing component (A) and component (B),

mixing components (A) and (B).

wherein components (A) and (B) are defined as described in any of claims 8 to 11 above.

14. Use of an initiator as described in any of claims 1 to 4 for starting the curing process of a cationic polymerizable substance.

15. Use of the curable composition as described in any of claims 9 or 11 for coating, sealing, moulding, adhering, making impressions.

16. Use of the curable composition as described in any of claims 9 or 11 for producing dental materials selected from precision impression materials, situation impression materials, bite registration materials, duplicating materials or modelling materials.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2006/029311

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L71/02 C08K5/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G C08L C08K

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

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

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 197 53 456 A1 (ESPE DENTAL AG, 82229 SEEFELD, DE) 10 June 1999 (1999-06-10) the whole document	1-16
A	US 4 167 618 A (SCHMITT ET AL) 11 September 1979 (1979-09-11) the whole document	1-16
A	WO 01/17483 A (ESPE DENTAL AG; ZECH, JOACHIM; ECKHARDT, GUNTHER; FUEHRER, CORNELIA; G) 15 March 2001 (2001-03-15) the whole document	1-16

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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

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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 January 2007	17/01/2007

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Kositza, Matthias

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2006/029311

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 19753456 A1	10-06-1999	NONE	
US 4167618 A	11-09-1979	NONE	
WO 0117483 A	15-03-2001	AT 345763 T	15-12-2006
		AU 772035 B2	08-04-2004
		AU 7282800 A	10-04-2001
		DE 19942459 A1	15-03-2001
		EP 1210055 A1	05-06-2002
		JP 2003508470 T	04-03-2003
		US 6894144 B1	17-05-2005