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(54) **Title:** STABLE CURABLE THIOL-ENE COMPOSITION

(57) **Abstract:** Curable composition comprising: A) at least one ethylenically or acetylenically unsaturated monomer or a mixture thereof; B) at least one thiol; D) at least one phosphonic acid; E) a component of the benzene or naphthalene series exhibiting at least one benzene ring or naphthalene ring containing at least two hydroxyl substituents.



Stable curable thiol-ene composition

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to curable or photocurable thiol-ene or thiol-yne compositions. Thiol-ene compositions comprise a thiol-component and an ene component, which is an ethylenically or acetylenically unsaturated monomer and are suited to be used in coating applications, adhesives, additive manufacturing technologies (AMT) and rapid prototyping (RP), in particular, suited for the production of three dimensional (3D) objects with the technique of stereolithography (SLA) and digital light processing (DLP). According to this definition, the term Thiol-ene compositions includes also Thiol-yne compositions.

Related Art

One of the best-known rapid prototyping processes, stereolithography (SLA), is widely spread and is often used in a broad field of technical applications nowadays, mainly within the aerospace, automotive and mechanical engineering industries. The technique of stereolithography uses a liquid photopolymer that is locally cured by a UV coherent or incoherent light source, like a laser or a UV lamp (see patent applications WO 2010/043559 and WO 2010/043275). The today standard stereolithographic resins are based on (meth)acrylate or epoxy photopolymers. (Meth)acrylate photopolymers exhibit relatively high shrinkage and oxygen inhibition whereas in epoxy photopolymers these drawback are avoided. However poor reactivity, high brittleness, sensitivity to moisture and high water uptake of the polymer are adverse effects.

An alternative to photopolymerization of (meth)acrylates and cationic monomers involves thiol-ene polymerization which has recently experienced a resurgence. Thiol-ene polymerizations, as opposed to simple (meth)acrylates, proceed rapidly to high conversions in air by a free-radical step growth process. Thiol-ene step growth radical polymerizations are based on the addition of a thiol to a vinyl functional group.

Thiol-ene polymers have recently reemerged on the industrial stage as an appropriate photopolymerizable material for SLA (see patent application WO 2010/043463). Various advantages such as rapid polymerization rates, minimal oxygen inhibition, near-complete polymerization and

lower shrinkage compared to the acrylate polymerizations make thiol-enes a suitable candidate for SLA technology.

Though thiol-ene materials exhibit many advantages, it is difficult to stabilize them, especially to attain long term shelf stability. Formulations which have long term shelf stability can be for example defined as those which do not double their viscosity in six months at room temperature. An increase in viscosity indicates that a spontaneous oligomerization reaction occurs between the polyene and polythiol. In extreme cases the unstable formulation will result in intractable insoluble gels.

Conventional free-radical stabilizers, such as hydroquinone, phenothiazine and the like, are commonly used as stabilizers for thiol-ene formulations, but it has long been recognized that such stabilizers often are not effective for providing a thiol-ene formulation with a commercially acceptable shelf life. Even with careful packaging to exclude any light, thiol-ene formulations often polymerize in their package within a few days of manufacture.

Despite remarkable advantages such as photoinitiatorless reactions, reduced oxygen sensitivity, fast polymerization rate and forming crosslinked networks with good physical and mechanical properties, thiol-ene systems show a limited shelf-life stability. All thiol-ene reactions exhibit spontaneous dark reactions, yielding polymers (oligomers) in the absence of initiator. The dark reaction takes place in the radiation curable formulations, in closed containers, usually resulting in premature polymerization. The storage stability of the thiol-ene system is affected by dark reaction at different extents, based on the activity of unsaturated enes and thiols.

Thiol-ene polymerization exhibits a number of advantages over conventional UV-curable resins, including inherently rapid reaction rate, reduced oxygen inhibition and reduced shrinkage due to the thiol-ene step growth reaction. However, poor shelf-life stability restricts thiol-ene application. The spontaneous dark reaction of thiol-ene formulations with increasing viscosity and formation of oligomers is a significant disadvantage for practical application. Therefore, there is a need for an improved stabilized system for thiol-ene formulations.

It is an object of the present invention to at least partially overcome the disadvantages of the prior art.

It is an object of the invention, in particular, to provide a curable or photocurable thiol-ene composition, which is stable, exhibits a long shelf and pot life resulting in a limited increase of the viscosity during the storage time.

It is an object of the invention, in particular, to provide a photocurable stable thiol-ene composition with a long term shelf stability both at room temperature (25 °C) and at elevated temperature (65°C).

It is also an object of the invention to provide a photocurable stable thiol-ene composition with high reactivity and photosensitivity, which produces after curing 3D objects characterized by low shrinkage and brittleness and high notch impact strength.

The object of the present invention is solved according to the features of the following independent claims.

SUMMARY OF THE INVENTION

According to a first aspect of the invention a curable, preferably photocurable, composition is provided comprising:

- A)** at least one ethylenically or acetylenically unsaturated monomer, preferably one acrylate or methacrylate or allylether or alkyne or allylazine or a mixture thereof;
- B)** at least one thiol;
- D)** at least one phosphonic acid;
- E)** a component of the benzene or naphthalene series exhibiting at least one benzene ring or naphthalene ring containing at least two hydroxyl substituents, preferably an optionally substituted polyhydroxybenzene.

A surprising synergistic effect was found by the addition of the free radical stabilizer E in combination with the acidic compound D in the composition. The composition can be curable by heat, but is preferably photocurable, being curable by actinic radiation or ultraviolet light (UV).

In a preferred embodiment the curable or photocurable composition comprises:

- A)** at least one ethylenically or acetylenically unsaturated monomer or a mixture thereof;
- B)** at least one thiol;
- C)** at least one radical photoinitiator;
- D)** at least one phosphonic acid;

- E)** a component of the benzene or naphthalene series exhibiting at least one benzene ring or naphthalene ring containing at least two hydroxyl substituents attached to the benzene ring or naphthalene ring.

In a preferred embodiment the component **E** exhibits the following structure (1):



(1)

wherein n is an integer from 2 to 6, m is an integer from 0 to $(6-n)$ and R_m are independently from each other organic radicals, preferably a C1-C6 alkyl.

Most preferably, n is 2, 3 or 4 and m is 0 or 1 in the structure (1) of component **E**

According to a particular embodiment of the invention the curable or photocurable composition comprises:

- A) 25 – 98 %, preferably 50 – 95 % by weight of component **A**;
- B) 1 – 70 %, preferably 3 – 40 % by weight of component **B**;
- C) 0 – 10 %, preferably 1 – 7 % by weight of component **C**;
- D) 0.01 – 10 %, preferably 0.5 – 5 % by weight of component **D**;
- E) 0.01 – 10 %, preferably 0.01 – 3 % by weight of component **E**;

each based on the total weight of the composition.

According to another embodiment of the invention the curable composition comprises:

- A) 60 – 90 % by weight of component **A**;
- B) 5 – 40 % by weight of component **B**;
- C) 1 – 5 % by weight of component **C**;
- D) 1 – 4 % by weight of component **D**;
- E) 0.05 – 2 % by weight of component **E**;

each based on the total weight of the composition.

In one embodiment of the present invention, the photocurable composition comprises 25 – 98 %, preferably 50 – 95 %, most preferably 60 – 90 % by weight of component **A**, based on the total weight of the composition.

In another embodiment of the present invention, the photocurable composition comprises 1 – 70 %, preferably 3 – 40 %, most preferably 5 – 40 % by weight of component **B**, based on the total weight of the composition.

In another embodiment of the present invention, the photocurable composition comprises 0 – 10 %, preferably 1 – 7 %, most preferably 1 – 5 % by weight of component **C**, based on the total weight of the composition.

In another embodiment of the present invention, the photocurable composition comprises 0.01 – 10 %, preferably 0.5 – 5 % most preferably 1 – 4 % by weight of component **D**, based on the total weight of the composition.

In another embodiment of the present invention, the photocurable composition comprises 0.01 – 10 %, preferably 0.01 – 3 %, most preferably 0.05 – 2 % by weight of component **E**, based on the total weight of the composition.

According to a preferred embodiment of the invention component **E** exhibits at least one benzene ring or naphthalene ring with two, three or four hydroxyl substituents bonded directly to said benzene ring or naphthalene ring .

According to another preferred embodiment of the invention component **E** comprises an optionally substituted benzene diol, benzene triol or pyrogallol.

According to another preferred embodiment of the invention component **D** comprises phenylphosphonic acid, vinylphosphonic acid, octanedisphonic acid or 2-Propenoic acid, 2-[(2-phosphonoethoxy)methyl]-1-ethyl ester (also called Ethyl 2-[4-(dihydroxyphosphoryl)-2-oxa-butyl]acrylate).

According to a preferred embodiment of the invention component **B** is a polythiol exhibiting from 2 to 4 SH groups.

According to a preferred embodiment of the invention component **B** comprises pentaerythritol tetra (3-mercaptopropionate), glycol di-3-mercaptopropionate, trimethylolpropane Tri-3-mercaptopropionate or pentaerythritol tetra (3-mercaptobutylate).

According to a preferred embodiment of the invention component **A** comprises diacrylates or dimethacrylates, in particular, 1,6-Hexane diol diacrylate or Bisphenol A ethoxylated di(meth)acrylate.

According to a preferred embodiment of the invention the viscosity of the photocurable composition at 25°C after 76 or 110 days at 65°C remains lower than 3.5 times, preferably lower than 2.5 times, most preferably lower than 2 times, the initial viscosity of the composition at 25°C.

According to a second aspect of the invention a process for producing a three- dimensional article in sequential cross-sectional layers in accordance with a model of the article is provided comprising the following steps:

- forming a first layer of a photocurable composition according to the invention;
- exposing the first layer to actinic radiation in a pattern corresponding to a respective cross-sectional layer of the model sufficient to harden the first layer in the imaged area ;
- forming a second layer of a photocurable composition according to the invention above the hardened first layer;
- exposing the second layer to actinic radiation in a pattern corresponding to a respective cross-sectional layer of the model sufficient to harden the second layer in the imaged area ;
- and repeating the previous two steps to form successive layers as desired to form the three-dimensional articles.

The actinic radiation is preferably incoherent and generated by an ultraviolet (UV) lamp.

(A) Component A

According to the present invention, the curable composition comprises one component **A**, which can be for example one acrylate or methacrylate or allylether or alkyne or allylazine or a mixture thereof .

In the following paragraphs, suitable **acrylate components** for resin compositions according to the present invention are listed. An acrylate component may refer to a single acrylate compound

or to a mixture of different acrylate compounds. Suitable acrylate components can be monofunctional, difunctional or of higher functionality.

Monofunctional acrylates may be used to modify resin properties.

Examples of monofunctional acrylates include such as isobornyl acrylate, tetrahydrofurfuryl acrylate, ethoxylated phenyl acrylates, lauryl acrylate, stearyl acrylate, octyl acrylate, isodecyl acrylate, tridecyl acrylate, caprolactone acrylate, nonyl phenol acrylate, cyclic trimethylolpropane formal acrylate, methoxy polyethyleneglycol acrylates, methoxy polypropyleneglycol acrylates, hydroxyethyl acrylate, hydroxypropyl acrylate, glycidyl acrylate. This list is not exhaustive and in each case ethoxylation and / or propoxylation of those acrylates can be used to modify properties further.

According to a preferred embodiment of the invention, acrylates are difunctional. Examples of aliphatic or cycloaliphatic difunctional acrylates include tricyclodecane dimethanol diacrylate (Sartomer® 833s), dioxane glycerol diacrylate (Sartomer® CD 536), 1,6 hexanediol diacrylate (Sartomer® 238), 3-methyl 1, 5-pentanediol diacrylate (Sartomer® 341), tripropylene glycol diacrylate (Sartomer® 306), Neopentyl glycol diacrylate (Sartomer® 247), dimethyloltricyclodecane diacrylate (Kayarad R-684), 1,4-dihydroxymethylcyclohexane diacrylate, 2,2-bis(4-hydroxy-cyclohexyl)propane diacrylate, bis(4-hydroxycyclohexyl)methane diacrylate. Examples of acyclic aliphatic difunctional acrylates include compounds of the formulae (F-I) to (F-IV) of U.S. Patent No. 6,413,697, herein incorporated by reference. Further examples of possible difunctional acrylates are compounds of the formulae (F-V) to (F-VIII) of U.S. Patent No. 6,413,697. Their preparation is also described in EP-A-0 646 580, herein incorporated by reference. Some compounds of the formulae (F-I) to (F-VIII) are commercially available. This list is not exhaustive and in each case ethoxylation and / or propoxylation of those diacrylates can be used to modify properties further.

Examples of aromatic difunctional acrylates include bisphenol A polyethylene glycol diether diacrylate (Kayarad R-551), 2,2'-methylenebis[p-phenylenepoly(oxyethylene)oxy]diethyl diacrylate (Kayarad R-712), hydroquinone diacrylate, 4,4'-dihydroxybiphenyl diacrylate, Bisphenol A diacrylate, Bisphenol F diacrylate, Bisphenol S diacrylate, ethoxylated or propoxylated Bisphenol A diacrylate, ethoxylated or propoxylated Bisphenol F diacrylate, ethoxylated or propoxylated Bisphenol S diacrylate, bisphenol-A epoxy diacrylate (Ebecryl® 3700 UCB Surface Specialties).

Examples of preferred polyethyleneglycol difunctional acrylates used in resins according to the invention are tetraethyleneglycol diacrylate (Sartomer® 268), polyethleneglycol(200) diacrylate (Sartomer® 259), polyethleneglycol(400) diacrylate (Sartomer® 344). This list is not exhaustive and in each case ethoxylation and / or propoxylation of those diacrylates can be used to modify properties further.

Examples of trifunctional acrylates or acrylate with even higher functionality are hexane-2,4,6-triol triacrylate, glycerol triacrylate, 1,1,1-trimethylolpropane triacrylate, ethoxylated or propoxylated glycerol triacrylate, ethoxylated or propoxylated 1,1,1-trimethylolpropane triacrylate, pentaerythritol tetraacrylate, bistrimethylolpropane tetraacrylate, pentaerythritol monohydroxytriacrylate, dipentaerythritol monohydroxypentaacrylate, dipentaerythritol pentaacrylate (Sartomer® 399), pentaerythritol triacrylate (Sartomer® 444), pentaerythritol tetracrylate (Sartomer® 295), trimethylolpropane triacrylate (Sartomer® 351), tris(2-acryloxy ethyl) isocyanurate triacrylate (Sartomer® 368), ethoxylated (3) trimethylolpropane triacrylate (Sartomer® 454), dipentaerythritol pentaacrylate ester (Sartomer® 9041). Examples of suitable aromatic triacrylates are the reaction products of triglycidyl ethers of trihydric phenols, and phenol or cresol novolaks containing three hydroxyl groups, with acrylic acid. This list is not exhaustive and in each case ethoxylation and / or propoxylation of those triacrylates can be used to modify properties further.

A polyacrylate may also be a polyfunctional urethane acrylate. Urethane acrylates may be prepared by, e.g., reacting a hydroxyl-terminated polyurethane with acrylic acid, or by reacting an isocyanate-terminated prepolymer with hydroxyalkyl acrylates to give the urethane acrylate. Preferred are urethane acrylates made from polyester diols, aliphatic isocyanates and hydroxyalkyl acrylates. Also preferred are those having polyfunctionality of acrylates or mixed acrylic and methacrylic functionality.

Furthermore, higher functionality acrylates, including hyperbranched polyester types, may also be used for resin modification. Commercially available examples include such as CN2301, CN2302, CN2303, CN2304 from Sartomer.

Additional examples of acrylates can be used in the formulation include such as D-310, D-330, DPHA-2H, DPHA-2C, DPHA-21, DPCA-20, DPCA-30, DPCA-60, DPCA-120, DN-0075, DN-2475, T-2020, T-2040, TPA-320, TPA-330 T-1420, PET-30, THE-330 and RP-1040 from

Kayarad, R-526, R-604, R-011, R-300 and R-205 from Nippon Kayaku Co. Ltd., Aronix M-210, M-220, M-233, M-240, M-215, M-305, M-309, M-310, M-315, M-325, M-400, M-6200 and M-6400 from Toagosei Chemical Industry Co, Ltd., Light acrylate BP-4EA, BP-4PA, BP-2EA, BP-2PA and DCP-A from Kyoeisha Chemical Industry Co.Ltd., New Frontier BPE-4, TEICA, BR-42M and GX-8345 from Daichi Kogyo Seiyaku Co.Ltd., ASF-400 from Nippon Steel Chemical Co.Ltd., Ripoxy SP-1506, SP-1507, SP-1509, VR-77, SP-4010 and SP-4060 from Showa Highpolymer Co.Ltd., NK Ester A-BPE-4 from Shin-Nakamura Chemical Industry Co.Ltd., SA-1002 from Mitsubishi Chemical Co.Ltd., Viscoat-195, Viscoat-230, Viscoat-260, Viscoat-310, Viscoat-214HP, Viscoat-295, Viscoat-300, Viscoat-360, Viscoat-GPT, Viscoat-400, Viscoat-700, Viscoat-540, Viscoat-3000 and Viscoat-3700 from Osaka Organic Chemical Industry Co.Ltd

In the following, suitable **methacrylate components** for resin compositions according to the present invention are listed. A methacrylate component may refer to a single methacrylate compound or to a mixture of different methacrylate compounds. Suitable methacrylate components can be monofunctional, difunctional or of higher functionality.

Monofunctional methacrylates may be used to modify resin properties.

Examples of monofunctional methacrylate include isobornyl methacrylate, tetrahydrofurfuryl methacrylate, ethoxylated phenyl methacrylate, lauryl methacrylate, stearyl methacrylate, octyl methacrylate, isodecyl methacrylate, tridecyl methacrylate, caprolactone methacrylate, nonyl phenol methacrylate, cyclic trimethylolpropane formal methacrylate, methoxy polyethyleneglycol methacrylates, methoxy polypropyleneglycol methacrylates, hydroxyethyl methacrylate, hydroxypropyl methacrylate, glycidyl methacrylate. This list is not exhaustive and in each case ethoxylation and / or propoxylation of those methacrylates can be used to modify properties further

Examples of aliphatic or cycloaliphatic difunctional methacrylates include 1,4-dihydroxymethylcyclohexane dimethacrylate, 2,2-bis(4-hydroxy-cyclohexyl)propane dimethacrylate, bis(4-hydroxycyclohexyl)methane dimethacrylate.

Examples of acyclic aliphatic difunctional methacrylates include compounds of the formulae (F-I) to (F-IV) of U.S. Patent No. 6,413,697, herein incorporated by reference. Further examples of possible dimethacrylates are compounds of the formulae (F-V) to (F-VIII) of U.S. Patent No. 6,413,697. Their preparation is also described in EP-A-0 646 580, herein incorporated by reference. Some compounds of the formulae (F-I) to (F-VIII) are commercially available. This

list is not exhaustive and in each case ethoxylation and / or propoxylation of those dimethacrylates can be used to modify properties further

Examples of preferred aromatic difunctional methacrylates used in resins according to the invention include ethoxylated (2) bisphenol A dimethacrylate (Sartomer ® 101K), ethoxylated (2) bisphenol A dimethacrylate (**Sartomer ® 348L**), ethoxylated (3) bisphenol A dimethacrylate (Sartomer ® 348C), ethoxylated (4) bisphenol A dimethacrylate (Sartomer ® 150), ethoxylated (4) bisphenol A dimethacrylate (Sartomer ® 540), ethoxylated (10) bisphenol A dimethacrylate (Sartomer ® 480), hydroquinone dimethacrylate, 4,4'-dihydroxybiphenyl dimethacrylate, Bisphenol A dimethacrylate, Bisphenol F dimethacrylate, Bisphenol S dimethacrylate, ethoxylated or propoxylated Bisphenol A dimethacrylate, ethoxylated or propoxylated Bisphenol F dimethacrylate, and ethoxylated or propoxylated Bisphenol S dimethacrylate.

Examples of trifunctional methacrylates or a methacrylate with even higher functionality include such as tricyclodecane dimethanol dimethacrylate (Sartomer ® 834), trimethylolpropane trimethacrylate (Sartomer® 350), tetramethylolmethane tetramethacrylate (Sartomer ® 367), hexane-2,4,6-triol trimethacrylate, glycerol trimethacrylate, 1,1,1-trimethylolpropane trimethacrylate, ethoxylated or propoxylated glycerol trimethacrylate, ethoxylated or propoxylated 1,1,1-trimethylolpropane trimethacrylate, pentaerythritol tetramethacrylate, bistrimethylolpropane tetramethacrylate, pentaerythritol monohydroxytrimethacrylate, dipentaerythritol monohydroxypentamethacrylate, Examples of suitable aromatic trifunctional methacrylates are the reaction products of triglycidyl ethers of trihydric phenols, and phenol or cresol novolaks containing three hydroxyl groups, with methacrylic acid. This list is not exhaustive and in each case ethoxylation and / or propoxylation of those methacrylates can be used to modify properties further. Examples of suitable aromatic trimethacrylates are the reaction products of triglycidyl ethers of trihydric phenols, and phenol or cresol novolaks containing three hydroxyl groups, with methacrylic acid.

Polymethacrylates may be used. A polymethacrylate may be a polyfunctional urethane methacrylate. Urethane methacrylates may be prepared by, e.g., reacting a hydroxyl-terminated polyurethane with methacrylic acid, or by reacting an isocyanate-terminated prepolymer with hydroxyalkyl methacrylates to give the urethane methacrylate. Preferred are urethane methacrylates made from polyester diols, aliphatic isocyanates and hydroxyalkyl methacrylates.

Also preferred are those having polyfunctionality of methacrylates or mixed acrylic and methacrylic functionality.

Examples of preferred aliphatic urethane methacrylates used in resins according to the invention include Genomer® 4205, Genomer® 4256 and Genomer® 4297.

Furthermore, higher functionality methacrylates, including hyperbranched polyester types, may also be used for resin modification.

Examples of **allylethers**, which could be used as component A in the curable composition according to the present invention, are monomers containing one or more allyl ether groups, which typically are bonded to a core structural group which can be based on a wide variety of polyhydric alcohols. Non-limiting examples of suitable polyhydric alcohols include neopentyl glycol, trimethylolpropane, ethylene glycol, propylene glycol, butylene glycol, diethylene glycol, trimethylene glycol, Methylene glycol, trimethylolethane, pentaerythritol, glycerol, diglycerol, 1,4-butanediol, 1,6-hexanediol, 1,4-cyclohexanedimethanol. Other exemplary allyl ether monomers include hydroxyethyl allyl ether, hydroxypropyl allyl ether, trimethylolpropane monoallyl ether, trimethylolpropane diallyl ether, triethylolethane monoallyl ether, trimethylolethane diallyl ether, glycerol monoallyl ether, glycerol diallyl ether, pentaerythritol monoallyl ether, pentaerythritol diallyl ether, pentaerythritol triallyl ether, 1,2,6-hexanetriol monoallyl ether, 1,2,6-hexanetriol diallyl ether, and the like. A preferred allylether is pentaerythritolallylether.

Examples of **alkynes**, which could be used as component A in the curable composition according to the present invention, include phenylacetylene, 1-hexyne, 1-octyne, 1-decyne, 1,5-hexadiyne, 1,7-octadiyne, 3,3-dimethyl-1-butyne, propargyl chloride, propargyl bromide, propargyl alcohol, 3-butyne-1-ol, 1-octyn-3-ol, methyl propargyl ether, propargyl ether, 3-methoxy-3-methyl-1-butyne, 2-methyl-3-butyne-2-ol, 1-ethynylcyclohexylamine, mono-propargylamine, 1-dimethylamino-2-propyne, tripropargylamine, 3-butyne-2-one, propiolic acid, 1-ethynyl-1-cyclohexanol, methyl propiolate, and trimethylsilylacetylene, 2-pentyne, 4-octyne, 2-butyne-1,4-diol, 3-hexyne-2,5-diol, and 1-phenyl-1-butyne. A preferred alkyne is 1,7-octadiyne.

Also well-suited compounds to be used as component A in the curable composition according to the present invention are compounds of the type cyanuric acid triallyl ester, triallyl triazine trione and the like. A preferred compound is triallyl triazine trione (TATATO).

(B) Component B (Thiol)

According to the present invention, the curable composition comprises at least one thiol component **B**.

The resin composition comprises at least a monofunctional or multifunctional thiol.

Multifunctional thiol means a thiol with two or more thiol groups. A multifunctional thiol may be a mixture of different multifunctional thiols.

A multifunctional thiol component of the inventive compositions may be any compound having two or more thiol groups per molecule. Suitable multifunctional thiols are described in U.S. Pat. No. 3,661,744 at Col. 8, line 76-Col. 9, line 46; in U.S. Pat. No. 4,119,617, Col. 7, lines 40-57; U.S. Pat. Nos. 3,445,419; and 4,289,867. Especially preferred are multifunctional thiols obtained by esterification of a polyol with an α - or β -mercaptocarboxylic acid such as thioglycolic acid, or β -mercaptopropionic acid.

Examples of preferred thiols used in compositions according to the present invention include pentaerythritol tetra-(3-mercaptopropionate) (**PETMP**), pentaerythritol tetrakis(3-mercaptobutylate) (**PETMB**), trimethylolpropane tri-(3-mercaptopropionate) (**TMPMP**), glycol di-(3-mercaptopropionate) (**GDMP**), pentaerythritol tetramercaptoacetate (**PETMA**), trimethylolpropane trimercaptoacetate (**TMPMA**), glycol dimercaptoacetate (**GDMA**), ethoxylated trimethylpropane tri(3-mercapto-propionate) 700 (**ETTMP 700**), ethoxylated trimethylpropane tri(3-mercapto-propionate) 1300 (**ETTMP 1300**), propylene glycol 3-mercaptopropionate 800 (**PPGMP 800**), propylene glycol 3-mercaptopropionate 2200 (**PPGMP 2200**).

(C) Component C (radical photoinitiator)

According to the present invention, the curable composition is preferably photocurable and comprises preferably at least a radical photo initiator.

The radical photo initiator can be a photo initiating system comprising a combination of different photo initiators and/or sensitizers. The photo initiating system can, however, be also a system comprising a combination of different compounds, which do not exhibit any photo initiating

property when taken alone, but which do exhibit photo initiating properties when combined together.

The photo initiator may be chosen from those commonly used to initiate radical photo polymerization.

Examples of free radical photo initiators include benzoin, benzoin ethers such as benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin phenyl ether, and benzoin acetate; acetophenones, e.g., acetophenone, 2,2-dimethoxyacetophenone, and 1,1-dichloroacetophenone; benzil ketals, e.g., benzil dimethylketal and benzil diethyl ketal; anthraquinones, e.g., 2-methylantraquinone, 2-ethylantraquinone, 2-tertbutylantraquinone, 1-chloroanthraquinone and 2-amylantraquinone; triphenylphosphine; benzoylphosphine oxides, e.g., 2,4,6-trimethylbenzoyl-diphenylphosphine oxide (**Lucirin ® TPO**); bisacylphosphine oxides; benzophenones, e.g., benzophenone and 4,4'-bis(N,N'-di-methylamino)benzophenone; thioxanthenes and xanthenes; acridine derivatives; phenazine derivatives; quinoxaline derivatives; 1-phenyl-1,2-propanedione 2-O-benzoyl oxime; 4-(2-hydroxyethoxy)phenyl-(2-propyl)ketone (Irgacure 2959; Ciba Specialty Chemicals); 1-aminophenyl ketones or 1-hydroxy phenyl ketones, e.g., 1-hydroxycyclohexyl phenyl ketone (**Irgacure ® 184**), 2-hydroxyisopropyl phenyl ketone, phenyl 1-hydroxyisopropyl ketone, and 4-isopropylphenyl 1-hydroxyisopropyl ketone. In so called Type II photoinitiators such as benzophenone or thioxanthone a coinitiator is generally required that is usually based on tertiary amine.

For this application, the radical photo initiators are preferably selected and their concentrations are preferably adjusted to achieve an absorption capacity such that the depth of cure is from about 0.05 to about 2.5 mm.

(D) Component D (phosphonic acid)

According to the present invention, the curable composition comprises at least one phosphonic acid D. Examples of phosphonic acids are alkylphosphonic acid, benzylphosphonic acid, arylphosphonic acid or phosphonic acid bearing a polymerizable substituent. Examples of preferred phosphonic acids are vinylphosphonic acid (**VP**), phenylphosphonic acid (**PPA**), 2-Propenoic acid, 2-[(2-phosphonoethoxy)methyl]-1-ethyl ester also called Ethyl 2-[4-(dihydroxyphosphoryl)-2-oxa-butyl]acrylate (**MA** or **MA154**).

(E) Component E

According to the present invention, the curable composition comprises at least one component E, which is a component of the benzene or naphthalene series exhibiting at least one benzene ring or naphthalene ring containing at least two hydroxyl substituents.

The at least two hydroxyl substituents are preferably directly attached to the benzene ring or naphthalene ring.

Component E exhibits preferably the following structure (1):



(1)

wherein n is an integer from 2 to 6, m is an integer from 0 to $(6-n)$ and R_m are, independently from each other, organic radicals, preferably a C1-C6 alkyl.

Most preferably, n is 2, 3 or 4 and m is 0 or 1 in the structure (1) of component E.

Component E exhibits preferably at least one benzene ring or naphthalene ring with two, three or four hydroxyl substituents bonded directly to said benzene ring or naphthalene ring.

Component E comprises preferably an optionally substituted benzene diol, benzene triol or pyrogallol.

Examples of specific possible compounds used as component E are: pyrogallol (**PRA**), 4-tert-butyl-1,2-dihydroxybenzene (**BDB**).

The composition can contain additional ingredients. Examples of additional ingredients include, but are not limited to, light stabilizers; sensitizers; antioxidants; fillers, such as reinforcing fillers, extending fillers, and conductive fillers; adhesion promoters; and fluorescent dyes.

DETAILED DESCRIPTION OF EMBODIMENTS

Several examples of curable compositions according to the invention and comparative examples have been produced.

Table I shows the trade name, the supplier and the chemical name of each component used to produce examples of curable compositions according to the invention and comparative examples (see Table II A to Table II F).

Trade Name	Supplier	Chemical Name
Component A:		
Sartomer SR348L	Cray Valley / Sartomer	Ethoxylated (2) Bisphenol A dimethacrylate
HDDA	Aldrich	1,6-Hexanediol diacrylate
Sartomer SR 349	Cray Valley / Sartomer	Ethoxylated (3) Bisphenol A diacrylate
Sartomer SR 9035	Cray Valley / Sartomer	Ethoxylated (15) trimethylolpropane triacrylate
Ebecryl 8402	Cytec	Aliphatic urethane diacrylate
pentaerythritol allylether	Aldrich	pentaerythritol allylether
1,7-octadiyne	Aldrich	1,7-octadiyne
TAICROS	Evonik	Triallyl triazinetriene
Component B:		
Thiocure PETMP	Bruno Bock	Pentaerythritol tetrakis(3-mercaptopropionate)
Thiocure TMPMP	Bruno Bock	Trimethylol-propane Tri-(3-mercapto-propionate)
Thiocure GDMP	Bruno Bock	Glycol Di-(3-mercapto-propionate)
Karenz MT-PEI	Showa Denko	Pentaerythritoltetrakis(3-mercaptopbutylate)
Component C:		
Irgacure 184	Ciba Specialty Chemicals	1-hydroxycyclohexyl-phenyl ketone
Irgacure 651	Ciba Specialty Chemicals	2,2-Dimethoxy-1,2-diphenylethan-1-one
Lucirin TPO	BASF	2,4,6-Trimethylbenzoyldiphenylphosphine oxide
Component D:		
PPA	Aldrich	Phenylphosphonic Acid
VP	Aldrich	Vinylphosphonic Acid
MA154	Ivoclar Vivadent	2-Propenoic acid, 2-[(2-phosphonoethoxy)methyl]-1-ethyl ester or (Ethyl 2-[4-(dihydroxyphosphoryl)-2-oxa-butyl]acrylate
Other organic acids:		
BA	Aldrich	Benzoic Acid
BSA	Aldrich	Benzene sulfonic Acid
Component E:		
PRA	Aldrich	Pyrogallol or 1,2,3-Trihydroxybenzene
BDB	Aldrich	4-tert-butyl-1,2-dihydroxybenzene
Other phenols:		
MP	Aldrich	4-methoxyphenol

Table I: components of compositions in Table II A to Table II F

Preparation of the compositions:

The curable compositions of the formulations which were studied are described in Table II A to Table II F (Examples 1 to 32). The percent in weight (wt%), based on the total weight of the composition, is indicated for all components in Table II A to Table II F.

Table II A describes examples 1 to 14, which are photocurable thiol-ene compositions comprising a radical photoinitiator and different phenols in combination or not with a phosphonic acid.

Table II B describes examples 15 to 18, which are photocurable thiol-ene compositions comprising a radical photoinitiator, pyrogallol in combination with phosphonic and not phosphonic acids.

Table II C describes examples 19 to 23, which are photocurable thiol-ene compositions comprising a radical photoinitiator, pyrogallol, a phosphonic acid, and different concentrations of Pentaerythritol tetrakis(3-mercaptopropionate).

Table II D describes examples 24 to 26, which are photocurable thiol-ene compositions comprising a radical photoinitiator, pyrogallol, a phosphonic acid, and different thiols.

Table II E describes examples 27 to 28, which are photocurable thiol-ene compositions comprising different (meth)acrylates, different radical photoinitiators, pyrogallol, and different phosphonic acids.

Table II F describes examples 29 to 32, which are photocurable thiol-ene compositions comprising a radical photoinitiator, pyrogallol (except example 32), a phosphonic acid, and pentaerythritol allylether or 1,7-octadiyne or Triallyltriazinetrione.

The photocurable compositions were prepared by addition of component D (phosphonic acid), E (phenolic component) and C (photoinitiator) to a 50 x 15 mm glass bottle. Next component A was added and the bottle was placed in an ultrasonic bath at 40°C. The bottle was occasionally removed from the ultrasonic bath and shaken for a few minutes until all the solids were completely dissolved. The mixture was cooled to room temperature and then component B was added and mixed for a few minutes. The glass bottles were then sealed and aged at room temperature (25 °C) or at 65°C. The whole process was carried out excluding actinic radiation and under a normal atmosphere. Viscosity measurements were performed at 25 °C just after preparation and periodically within the storage time.

Viscosity measurements:

One of the marked effects of instability is gelling and thus one expects the viscosity of a formulation to increase until it gels. Therefore, stability of the thiol-ene formulations was investigated by following the change in viscosity with time.

A Modular Compact Rheometer Physica MCR 300 was used for measuring the viscosity. For all tests, a cone-on-plate geometry was used with a cone angle of 1° and a cone diameter of 25 mm. The tests were always performed at a constant temperature of **25°C**. The viscosity was tested in decreasing shear rates from 150 s^{-1} to 10 s^{-1} , over a period of 75 s, taking measurement every 5 s. This resulted in 15 measurement points. The viscosity was measured under shear rate of 100 s^{-1} . The measurements were performed with 0.1 ml of samples and with accuracy of about $\pm 3.5 \%$.

The prepared formulations were kept at ambient temperature in a room with yellow light. This should avoid the light-induced polymerization. The viscosity measurements were performed at 25°C at storage time zero just after the preparation, and within a number of days between 4 and 110 after a storage time at room temperature (25 °C) or at 65°C.

The results of viscosity measurements are reported in Table III A to Table III F for the photocurable compositions described in Table II A to Table II F (examples 1 to 32).

The definition of an acceptable viscosity increase of the thiol-ene photocurable compositions during the ageing time depends from the applications. Since ageing test at room temperature (25°C) would take too long time, accelerated ageing tests at 65°C are considered, in order to evaluate the stability of the photocurable composition as a function of the ageing time. If the viscosity of the photocurable composition at 25°C after 76-79 days at 65°C remains lower than 3.5 times, preferably 2.5 times the initial viscosity of the photocurable composition at 25°C, such photocurable composition can be defined as stable and can be considered suited for several stereolithography (SLA) applications, for example as photocurable resin for the stereolithography rapid prototyping equipments disclosed in WO 2010/043559 or WO 2010/043275.

In Table III A comparative examples 1, 2, 4, 7, 9, 11 to 14 show that the photocurable thiol-ene composition is not stable and a dramatic viscosity increase or even gelling occurs after 76 days at 65°C.

In Table III A inventive example 3 shows that the photocurable thiol-ene composition is surprisingly and unexpectedly stabilized by the synergetic effect of the combination of pyrogallol

with phosphonic acid, and only a slight viscosity increase (from 0.99 to 1.64 Pa·s) occurs after 76 days at 65°C. Example 3 must be compared with example 1 and 2, which are similar compositions, but do not exhibit the favourable stabilising combination of pyrogallol with phosphonic acid.

In Table III A inventive example 5 shows that the photocurable thiol-ene composition is surprisingly and unexpectedly stabilized by the synergetic effect of the combination of pyrogallol with phosphonic acid also if the amount of pyrogallol is only 0.1 wt%, and only a slight viscosity increase (from 0.90 to 1.46 Pa·s) occurs after 76 days at 65°C. Example 5 must be compared with example 1 and 4, which are similar compositions, but do not exhibit the favourable stabilising combination of pyrogallol with phosphonic acid.

In Table III A inventive example 8 shows that the photocurable thiol-ene composition is surprisingly and unexpectedly stabilized by the synergetic effect of the combination of 4-tert-butyl-1,2-dihydroxybenzene with phosphonic acid, and only a slight viscosity increase (from 0.93 to 2.12 Pa·s) occurs after 76 days at 65°C. Example 8 must be compared with example 1 and 7, which are similar compositions, but do not exhibit the favourable stabilising combination of 4-tert-butyl-1,2-dihydroxybenzene with phosphonic acid.

In Table III B inventive examples 15 and 16 show that the photocurable thiol-ene composition is surprisingly and unexpectedly stabilized by the synergetic effect of the combination of pyrogallol with different types of phosphonic acids, and only a slight viscosity increase (respectively from 0.92 to 1.71 Pa·s and from 1.03 to 1.83 Pa·s) occurs after 76 days at 65°C. Examples 15 and 16 must be compared with comparative examples 17 and 18, which are similar compositions, but exhibit the combination of pyrogallol with non phosphonic acids.

In Table III C inventive examples 19 to 23 show that the photocurable thiol-ene composition is surprisingly and unexpectedly stabilized by the synergetic effect of the combination of pyrogallol with phosphonic acid, when the content of Pentaerythritol tetrakis(3-mercaptopropionate) is varied from 4 wt% to 34 wt%, and only a slight viscosity increase occurs after 79 days at 65°C.

In Table III D inventive examples 24 to 26 containing different types of thiols show that the photocurable thiol-ene composition is surprisingly and unexpectedly stabilized by the synergetic effect of the combination of pyrogallol with phosphonic acid for different types of thiols, and only a slight viscosity increase occurs after 79 days at 65°C.

In Table III E inventive examples 27 to 28 containing different types of (meth)acrylates show that the photocurable thiol-ene composition is surprisingly and unexpectedly stabilized by the synergetic effect of the combination of pyrogallol with phosphonic acid for different types of (meth)acrylates, and only a slight viscosity increase occurs after 76 days at 65°C (respectively from 1.84 to 4.01 Pa·s and from 1.89 to 3.64 Pa·s).

In Table III F inventive examples 29 to 31 containing different types of allylethers or alkynes or allylazines show that the photocurable thiol-ene composition is surprisingly and unexpectedly stabilized by the synergetic effect of the combination of pyrogallol with phosphonic acid for different types of allylethers or alkynes or allylazines, and only a slight viscosity increase occurs after 79 days at 65°C. Comparative example 32 exhibits the same composition as example 30 without pyrogallol and gelled after 1 day at 65°C.

Photocuring of the photocurable compositions:

The photocurable compositions according to the invention have been cured by the use of incoherent actinic radiation and ultraviolet (UV) radiation to produce three dimensional (3D) objects. The addition in the thiol-ene photocurable composition of the stabilizing system phosphonic acid/phenolic component changed neither the reactivity, the photosensitivity, the curing speed of the composition, nor the mechanical strength, the elastic modulus, the toughness of the produced 3D objects.

The specimens for notch impact strength test were produced using digital light processing (DLP). The 3D-parts were produced using a stereolithography equipment EnvisionTec Perfactory® SXGA+W/ERM Mini MultiLens with a resolution of 1400 x 1050. The specimens were built with an exposure time of 11 s for a layer thickness of 50 µm, at a lamp power of 800 mW/dm². After completion of the structuring process, the prototype was rinsed with ethanol, followed by 20 minutes post-curing (10 minutes per each side) under the UV lamp (INTELLI-RAY 600 Watt UV flood curing system.). The specimens were rectangular with a dimension of about 14/7/55 mm (width/ height /length) for notch impact strength.

Izod notched impact strength Tests:

Izod notched impact strength was evaluated using DLP-formed notched specimen. Tests were performed on a Zwick Model 5113.11 impact tester type machine, equipped with a hammer (Zwick Co., Germany), according to ISO 180 standards.

Table IV shows the results of the notch impact strength measurements on the cured composition 1 (comparative example) and on the inventive composition 5, cured immediately or after a storage time of 30 days at 65°C. The notch impact strength measurements show that the addition of the stabilizing system phosphonic acid/phenolic component did not impair at all the impact strength of the cured composition. Furthermore, the impact strength of the cured stabilized composition is not affected at all by an ageing time of 30 days at 65°C before curing.

Example Number	storage time at 65°C (days)	Viscosity (Pa·s)	acN [kJ/m²]	standard derivation [kJ/m²]	variance [%]
1	0	1.71	7.25	0.087	12.01
5	0	0.90	6.80	0.117	17.25
	30	1.34	6.54	0.024	3.73

Table IV: results of the notch impact strength measurements on cured composition 1 and 5

Example number	1 (wt%)	2 (wt%)	3 (wt%)	4 (wt%)	5 (wt%)	6 (wt%)	7 (wt%)	8 (wt%)	9 (wt%)	10 (wt%)	11 (wt%)	12 (wt%)	13 (wt%)	14 (wt%)
SR348L	61.8	62.37	61.17	62.94	61.74	61.80	62.18	60.99	62.92	61.72	62.37	61.17	62.94	61.74
PETMP	33.35	33.66	33.01	33.97	33.32	33.35	33.56	32.91	33.96	33.31	33.66	33.01	33.97	33.32
IRG184	2.95	2.97	2.92	2.99	2.94	2.94	2.96	2.90	2.99	2.94	2.97	2.92	2.99	2.94
PRA	-	1	1	0.1	0.1	0.01	-	-	-	-	-	-	-	-
BDB	-	-	-	-	-	-	1.3	1.3	0.13	0.13			-	-
MP	-	-	-	-	-	-	-	-	-	-	1	1	0.1	0.1
MA154	1.9	-	1.9	-	1.9	1.9	-	1.9	-	1.9		1.9	-	1.9
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100

Table II A: compositions with different phenolic components

Example number	15 (wt%)	16 (wt%)	17 (wt%)	18 (wt%)
SR348L	62.37	62.12	62.31	62.12
PETMP	33.66	33.52	33.63	33.52
IRG184	2.97	2.96	2.96	2.96
PRA	0.1	0.1	0.1	0.1
VP	0.9	-	-	-
PPA	-	1.3	-	-
BA	-	-	1	
BSA	-	-	-	1.3
Total	100	100	100	100

Table II B: compositions with phosphonic and non phosphonic acids

Example number	19 (wt%)	20 (wt%)	21 (wt%)	22 (wt%)	23 (wt%)
SR348L	61.86	69.14	80.11	87.02	90.93
PETMP	33.44	26.15	15.15	8.23	4.31
IRG184	2.85	2.85	2.85	2.85	2.85
PRA	0.1	0.1	0.1	0.1	0.1
MA154	1.75	1.76	1.79	1.80	1.81
Total	100	100	100	100	100

Table II C: compositions with different PETMP concentrations

Example number	24 (wt%)	25 (wt%)	26 (wt%)
SR348L	62.39	60.00	59.44
GDMP	32.88	-	-
TMPMP	-	35.27	-
Karenz PE1	-	-	35.82
IRG184	2.86	2.86	2.86
PRA	0.1	0.1	0.1
MA154	1.77	1.77	1.78
Total	100	100	100

Table II D: compositions with different thiols

Example number	27 (wt%)	28 (wt%)
SR348	31.7	31.91
SR349	18.1	18.22
SR9035	9.51	9.58
Ebecryl 8402	26.28	26.46
IRG651	1.31	1.32
Lucirin TPO	1.1	1.11
PETMP	10	10
PRA	0.1	0.1
PPA	-	1.3
MA154	1.9	-
Total (wt%)	100	100

Table II E: compositions with different (meth)acrylates

Example number	29 (wt%)	30 (wt%)	31 (wt%)	32 (wt%)
pentaerythritol allylether	39.62	-	-	-
1,7-octadiyne	-	28.81	-	29.45
Triallyltriazinetrione	-	-	38.60	-
PETMP	55.63	66.35	56.78	67.65
IRG184	2.86	2.86	2.86	2.90
PRA	0.1	0.1	0.1	-
MA154	1.79	1.88	1.66	-
Total (wt%)	100	100	100	100

Table II F: compositions with allylether or alkyne or allylazine

Example Number	Storage time (day)	at 25°C	at 65°C
		Viscosity (Pa ·s)	
1	Gel after 22 days at RT, and at 65 °C within 19 hours		
2	0	0.95	0.95
	21	1.00	2.48
	76	1.10	16.2
	110	1.10	35.65
3	0	0.99	0.99
	21	0.98	1.21
	76	0.97	1.64
	110	0.97	1.89
4	0	0.88	0.88
	20	0.95	5.85
	76	1.24	31.27
	110	1.54	solid
5	0	0.90	0.90
	20	0.90	1.08
	76	0.87	1.46
	110	0.88	1.71
6	0	0.89	
	245	3.15	
7	0	0.89	0.89
	20	0.95	7.11
	76	1.22	64.98
	110	1.40	solid

Example Number	Storage time (day)	at 25°C	at 65°C
		Viscosity (Pa ·s)	
8	0	0.93	0.93
	21	0.96	1.22
	76	0.95	2.12
	110	0.95	2.94
9	0	0.86	0.86
	21	1.04	9.72
	76	1.51	34.23
	110	1.831	solid
10	0	0.89	
	21	0.90	
	76	0.91	
	110	0.93	
11	0	0.89	0.89
	14	3.46	8.26
	22	4.51	16.52
	76	2.87	solid
12	0	0.85	0.85
	14	solid	solid
13	0	0.84	0.84
	14	23.63	solid
14	0	0.90	0.90
	14	1.74	solid
	22	solid	solid

Table III A: viscosity at 25°C as a function of ageing time at 25 and 65 °C for compositions in Table II A with different phenolic components

Example Number	Storage time (day) at 65°C	Viscosity (Pa·s)
15	0	0.92
	20	1.35
	76	1.71
	110	1.90
16	0	1.03
	26	1.52
	76	1.83
	110	2.05
17	0	0.92
	26	1.88
	76	5.04
	110	9.25
18	The gelation occurred after 3 hours	

Table III B: viscosity at 25°C as a function of ageing time at 65 °C for compositions in Table II B with phosphonic and non phosphonic acids

Example Number	Storage time (day) at 65°C	Viscosity (Pa·s)
19	0	1.05
	5	1.35
	26	1.32
	79	1.41
20	0	1.15
	5	1.60
	26	1.45
	79	1.73
21	0	1.35
	5	1.78
	26	1.46
	79	1.76
22	0	1.41
	5	1.95
	26	1.59
	79	1.67
23	0	1.50
	5	1.96
	26	1.40
	79	1.76

Table III C: viscosity at 25°C as a function of ageing time at 65 °C for compositions in Table II C with different PETMP concentrations

Example Number	Storage time (day) at 65°C	Viscosity (Pa·s)
24	0	0.14
	5	0.14
	26	0.19
	79	0.21
25	0	0.91
	5	1.19
	26	1.08
	79	1.05
26	0	1.3
	5	1.36
	26	1.48
	79	1.71

Table III D: viscosity at 25°C as a function of ageing time at 65 °C for compositions in Table II D with different thiols

Example Number	Storage time (day) at 65°C	Viscosity (Pa·s)
29	0	0.065
	5	0.11
	26	0.11
	79	0.15
30	0	0.016
	5	0.017
	26	0.020
	79	0.058
31	0	0.37
	5	0.79
	26	0.73
	79	1.17
32	0	0.016
	1	gelled

Table III F: viscosity at 25°C as a function of ageing time at 65 °C for compositions in Table II F with allylether or alkyne or allylazine

Example Number	Storage time (day)	at 25°C	at 65°C
		Viscosity (Pa·s)	
27	0	1.84	1.84
	20	1.84	2.35
	76	1.82	4.01
	110	1.85	6.30
28	0	1.85	1.89
	20	1.84	2.40
	76	1.83	3.64
	110	1.85	4.97

Table III E: viscosity at 25°C as a function of ageing time at 25 and 65 °C for compositions in Table II E with different (meth)acrylates

Claims

1. Curable composition comprising:
 - A) at least one ethylenically or acetylenically unsaturated monomer or a mixture thereof;
 - B) at least one thiol;
 - D) at least one phosphonic acid;
 - E) a component of the benzene or naphthalene series exhibiting at least one benzene ring or naphthalene ring containing at least two hydroxyl substituents.
2. Curable composition, preferably a photocurable composition, according to claim 1 comprising:
 - A) at least one ethylenically or or acetylenically unsaturated monomer or a mixture thereof;
 - B) at least one thiol;
 - C) at least one radical photoinitiator;
 - D) at least one phosphonic acid;
 - E) a component of the benzene or naphthalene series exhibiting at least one benzene ring or naphthalene ring containing at least two hydroxyl substituents attached to the benzene ring or naphthalene ring.
3. Curable composition, preferably a photocurable composition, according to claim 1 or 2, wherein component E exhibits the following structure (1):



(1)

wherein n is an integer from 2 to 6, m is an integer from 0 to $(6-n)$ and R_m are independently from each other organic radicals, preferably a C1-C6 alkyl.

4. Curable composition, preferably a photocurable composition, according to any of the preceding claims comprising:

- A) 25 – 98 %, preferably 50 – 95 % by weight of component **A**;
 - B) 1 – 70 %, preferably 3 – 40 % by weight of component **B**;
 - C) 0 – 10 %, preferably 1 – 7 % by weight of component **C**;
 - D) 0.01 – 10 %, preferably 0.5 – 5 % by weight of component **D**;
 - E) 0.01 – 10 %, preferably 0.01 – 3 % by weight of component **E**;
- each based on the total weight of the composition.

5. Curable composition according to any of the preceding claims comprising:

- A) 60 – 90 % by weight of component **A**;
 - B) 5 – 40 % by weight of component **B**;
 - C) 1 – 5 % by weight of component **C**;
 - D) 1 – 4 % by weight of component **D**;
 - E) 0.05 – 2 % by weight of component **E**;
- each based on the total weight of the composition.

6. Curable composition according to any of the preceding claims, wherein component **E** exhibits at least one benzene ring or naphthalene ring with two, three or four hydroxyl substituents bonded directly to said benzene ring or naphthalene ring.

7. Curable composition according to claim 3, wherein n is 2, 3 or 4 and m is 0 or 1 in the structure (1) of component **E**.

8. Curable composition according to any of the preceding claims, wherein component **E** comprises an optionally substituted benzene diol, benzene triol or pyrogallol.

9. Curable composition according to any of the preceding claims, wherein component **D** comprises phenylphosphonic acid, vinylphosphonic acid, octanedisphonic acid or 2-Propenoic acid, 2-[(2-phosphonoethoxy)methyl]-1-ethyl ester.

10. Curable composition according to any of the preceding claims, wherein component **B** is a polythiol exhibiting from 2 to 4 SH groups.

11. Curable composition according to any of the preceding claims, wherein component **B** comprises pentaerythritol tetra (3-mercaptopropionate), glycol di-3-Mercaptopropionate, trimethylolpropane tri-3-mercaptopropionate or pentaerythritol tetra (3-mercaptobutylate).
12. Curable composition according to any of the preceding claims, wherein component **A** comprises diacrylates or dimethacrylates, in particular, 1,6-Hexane diol diacrylate or Bisphenol A ethoxylated di(meth)acrylate.
13. Curable composition according to any of the preceding claims, wherein the viscosity of the composition at 25°C after 76 or 110 days at 65°C remains lower than 3.5 times, preferably lower than 2.5 times, the initial viscosity of the composition at 25°C.
14. A process for producing a three- dimensional article in sequential cross-sectional layers in accordance with a model of the article comprising the following steps:
:
 - forming a first layer of a photocurable composition according to any of the preceding claims;
 - exposing the first layer to actinic radiation in a pattern corresponding to a respective cross-sectional layer of the model sufficient to harden the first layer in the imaged area ;
 - forming a second layer of a photocurable composition according to any of the preceding claims above the hardened first layer;
 - exposing the second layer to actinic radiation in a pattern corresponding to a respective cross-sectional layer of the model sufficient to harden the second layer in the imaged area ;
 - and repeating the previous two steps to form successive layers as desired to form the three-dimensional articles.
15. Three- dimensional article produced according to the process of claim 14.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/053045

A. CLASSIFICATION OF SUBJECT MATTER
INV. G03F7/004 G03F7/027 G03F7/00
ADD.

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)
G03F

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 practicable, search terms used)

EPO-Internal, COMPENDEX, INSPEC, IBM-TDB, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 824 104 A (KLOCZEWSKI H ET AL) 16 July 1974 (1974-07-16)	1-8,10, 11,13
Y	column 5, paragraph 19-31 column 6, lines 31-41; example 2 -----	14,15
X	US 4 443 495 A (MORGAN CHARLES R [US] ET AL) 17 April 1984 (1984-04-17)	1,3-8, 10-13
Y	column 8, lines 14-20 column 9, lines 30-44; example 3 -----	14,15
X	US 3 925 320 A (MORGAN CHARLES R) 9 December 1975 (1975-12-09)	1-8,10, 11,13
Y	column 11, lines 40-46 column 17, lines 27-32; example 10 -----	14,15
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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 application or patent 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

9 May 2012

Date of mailing of the international search report

06/06/2012

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Oechsner de Coninck

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2012/053045

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 048 218 A (MORGAN CHARLES R ET AL) 13 September 1977 (1977-09-13)	1-8,10, 11,13
Y	Compositions A-C; column 13; example III -----	14,15
Y	EP 1 477 511 A1 (DSM IP ASSETS BV [NL]) 17 November 2004 (2004-11-17) paragraphs [0077], [0079] -----	14,15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2012/053045

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