
Sulfide-containing stabilizer system for thiol-ene and thiol-yne compositions

5 The invention relates to a stabilizer system according to Claim 1, the use of the stabilizer system according to Claim 9 and also a radiation-curable thiol-ene or thiol-yne composition according to Claim 11.

10 The reaction of thiols with unsaturated organic compounds was described for the first time in the literature in the year 1905 by Theodor Posner. Numerous comprehensive articles on this subject have been published up to the present day. The photochemical reaction of thiols with unsaturated organic compounds in particular is of current interest up to the present day since it allows quick curing of systems with a low energy input.

15 EP 2 588 448 B1 describes the use of thiol-ene and thiol-yne compositions for producing films containing light-emitting nanoparticles. EP 3 131 952 B1 describes the use of thiols together with alkynes for printable UV-crosslinkable resin systems. Further fields of use for radiation-curable thiol-ene and thiol-yne compositions are, for example, the production of gel nails, inks, coatings, adhesives and in the production of 3D objects by stereolithography or 3D printing.

20 In contrast to a homopolymerization of acrylates or methacrylates, the thiol-ene and thiol-yne reactions are characterized by being a step growth reaction rather than a chain growth reaction. As a result, more homogeneous networks are formed and, associated therewith, the polymer has less shrinkage and fewer inhomogeneities. The degree of conversion of the monomers is higher in the case of thiol-ene and thiol-yne polymerizations. A further advantage is the
25 insensitivity of the free-radical polymerization process to oxygen.

The thioether-based polymer structures have further interesting properties which cannot be obtained to the same extent by photopolymerization of acrylates and methacrylates. Thus, for example, US 8 440 736 B2 describes the particular barrier properties of thiol-ene films.

30 Thiols can be added onto unsaturated organic compounds such as alkenes or alkynes in a free-radical reaction. This type of reaction is also referred to as thiol-ene reaction in the case of alkenes and as thiol-yne reaction in the case of reaction with alkynes. The two reactions are known collectively by the term thiol click reaction. The free-radical polymerization can here be
35 triggered thermally and also photochemically, in particular with addition of one or more appropriate photoinitiators. Initiation purely by light without addition of a photoinitiator is also possible.

An alternative to the free-radical addition of thiols onto unsaturated organic compounds is the ionic thiol Michael addition. The product is likewise a thioether as is obtained by the free-radical mechanism. The thiol Michael addition is catalysed by bases or nucleophiles. Electrophilic unsaturated double bonds, as are present, for example, in acrylates and methacrylates, promote the thiol Michael addition.

A disadvantage of thiol-ene and thiol-yne compositions is that they are difficult to stabilize, in particular in order to achieve long-term storage stability. All thiol-ene and thiol-yne reactions display spontaneous dark reactions which in the absence of an initiator form polymers or at least oligomers if no effective stabilizer is added. These undesirable reactions during storage of thiol-ene and thiol-yne compositions, which are, in particular, kept in stock as premixed one-component systems, can lead to an increase in the viscosity or even to curing of the system.

WO 2011 155 239 A1 describes the use of substituted naphthalenes as stabilizers for thiol-ene compositions. WO 2012 126 695 A1 discloses the combination of phosphonic acid or acid phosphonic esters in combination with substituted benzene or naphthalene derivatives as stabilizer system for thiol-ene compositions. A disadvantage of these stabilizers or stabilizer systems is that it is not possible to achieve sufficient stabilization of a thiol-ene composition for commercial storage without hindering the desired reaction in use of the respective composition. The thiol-ene compositions are then storage-stable but cannot be cured satisfactorily by the selected methods. This hinders the commercial utility of the stabilizer systems used.

It is therefore an object of the invention to eliminate the disadvantages of the prior art and provide a stabilizer system for a thiol-ene and/or thiol-yne composition which stabilizes the latter sufficiently and does not hinder the use of the composition. The stabilizer system and also a thiol-ene or thiol-yne composition containing the stabilizer system should be able to be produced simply and inexpensively.

The main features of the invention are indicated in Claim 1. Embodiments are subject matter of Claims 2 to 12.

The object is achieved according to the invention by a stabilizer system, in particular for thiol-ene and/or thiol-yne compositions, comprising:

- at least one free-radical-scavenging component (A)
- at least one acid component (B), where the acid component (B) comprises one or more organic acids, and

- at least one sulfidic component (C) selected from the group consisting of organic sulfides.

5 When mention is made in the following of individual substances, compounds or components, a plurality of molecules can of course be assumed.

A thiol-ene or thiol-yne composition comprises at least one thiol component (D) which comprises, in particular, a dithiol and/or polythiol, and a component comprising at least one unsaturated carbon compound (E). Unsaturated organic compounds which have at least one
10 double bond between two carbon atoms joined to one another are referred to as alkenes. Unsaturated organic compounds having at least one triple bond between two carbon atoms joined to one another are referred to as alkynes. In particular, a thiol-ene composition thus comprises at least one thiol component and an alkene component. A thiol-yne composition comprises at least one thiol component and an alkyne component. In addition, a thiol-ene and
15 thiol-yne composition can comprise further constituents such as a stabilizer system and/or one or more photoinitiators.

The stabilizer system of the invention stabilizes a thiol-ene and/or thiol-yne composition so that premature reactions during storage are hindered or even prevented without the desired reaction
20 when use is made being adversely affected. The combination of the free-radical-scavenging components (A), the acid component (B) in the form of an organic acid and the sulfidic component (C) which consists of an organic sulfide brings about a synergy, so that improved stabilization of an in particular photoreactive thiol-ene and/or thiol-yne composition can be achieved. In addition, desired reactions in the form of curing by polymerization after use of the
25 thiol-ene are not hindered.

The **free-radical-scavenging component** (A) preferably comprises one or more free-radical scavengers selected from the following group: sterically hindered phenols, sterically hindered naphthalenes and sterically hindered amines.

30 Sterically hindered phenols as free-radical scavengers have as a basis at least one phenol ring in their structure. They are characterized by one or more further substituents such as hydroxyl, tert-butyl or methyl groups on at least one phenol ring. Sterically hindered, phenolic free-radical scavengers include, *inter alia*, pyrogallol (1,2,3-trihydroxybenzene) and esters thereof, gallic
35 acid and esters thereof, tocopherols and tert-butylhydroxyquinone.

Sterically hindered naphthalenes as free-radical scavengers have as a basis a condensed ring system in their structure. Like the sterically hindered phenols, at least one benzene rings bears one or more substituents such as hydroxyl, tert-butyl or methyl groups.

- 5 The **free-radical-scavenging component** (A) preferably comprises one of more of the following phenols: 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione, 2,2'-methylenebis(4-ethyl-6-tert-butylphenol), pentaerythritol tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], tetrakis[methylene-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionato]methane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, 10 hexamethylene bis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione, alpha-tocopherol, 2,6-di-tert-butyl-4-sec-butylphenol, 2,6-di-tert-butyl-4-nonylphenol, 2,5-di-tert-amylhydroquinone, 4,4'-butylidenebis(6-tert-butyl-m-cresol), 4,4',4''-(1-methylpropanyl-3-ylidene)tris[6-tert-butyl-m-cresol], 2,2'-methylenebis[6-(1-methylcyclohexyl)-p-cresol], ethylenebis(oxyethylene) bis[3-(5-tert-butyl-4-hydroxy-m-tolyl)propionate], poly(dicyclopentadiene-co-p-cresol), 6-tert-butyl-2,4-xlenol, 2,2'-(2-methylpropylidene)bis[4,6-xlenol], 2,6-di-tert-butyl-4-methylphenol, pyrogallol (1,2,3-trihydroxybenzene), propyl gallate (propyl 3,4,5-trihydroxybenzoate), C7-9-alkyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (CAS 125643-61-0).

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The free-radical-scavenging component (A) is particularly preferably 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione (CAS 40601-76-1), pyrogallol (1,2,3-trihydroxybenzene - CAS 87-66-1), propyl gallate (propyl 3,4,5-trihydroxybenzoate - CAS 121-79-9) or a combination thereof.

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In a preferred embodiment, the one or more organic acids of the acid component (B) have a pK_a in the range from 1 to 5.5 at 25°C. This is a sufficient acid strength to achieve a synergistic effect in the stabilization of a thiol-ene or thiol-yne composition by the stabilizer system. In one embodiment, the organic acids have a pK_a in the range from 3.5 to 5.5. Suitable acids are, for 30 example, methacrylic acid (pK_a 4.256), methacrylic acid (pK_a 4.66), lactic acid (pK_a 3.9), formic acid (pK_a 3.8), acetic acid (pK_a 4.75) and propionic acid (pK_a 4.87). In a further embodiment, the organic acids preferably have a pK_a in the range from 1 to 3. Suitable acids are, for example, organic acid esters of phosphoric acids, methacrylic esters of phosphoric acids or acidic acrylate and methacrylate derivatives.

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The **acid component** (B) preferably comprises one or more organic acids, in particular one or more unsaturated carboxylic acids or carboxylic acid derivatives, e.g. carboxylic acids bearing phosphonic acid groups. The acid component (B) particularly preferably comprises one or more

organic acids selected from the following group: methacrylic acid, acrylic acid and derivatives thereof and Ebecryl® 168, obtainable from Allnex USA Inc., which comprises an acidic methacrylate, Miramer SC1400, a phosphoric ester of a methacrylic acid derivative, from Miwon Specialty Chemical. The acid component (B) is particularly preferably methacrylic acid, acrylic acid, Ebecryl®168, Miramer® SC1400 or a mixture thereof.

In a preferred embodiment, the one or more organic sulfide(s) of the sulfidic component (C) have further functional units in the structure, in particular ester functions. These have been found to be particularly advantageous. In particular, the organic sulfides do not comprise any free thiols, acids and/or hydroxy functions.

The **sulfidic component (C)** used preferably comprises one or more organic sulfides selected from the following group: ditridecyl thiodipropionate, dilauryl thiodipropionate, distearyl thiodipropionate, dimethyl thiodipropionate, octadecyl 3-[[3-(dodecyloxy)-3-oxopropyl]thio]propionate, dimyristyl thiodipropionate, 2,2-bis[[3-(dodecylthio)-1-oxopropoxy]methyl]propane-1,3-diyl bis[3-(dodecylthio)propionate]. The sulfidic component (C) is particularly preferably ditridecyl thiodipropionate, dilauryl thiodipropionate or a combination thereof.

In a further development, the at least one free-radical-scavenging component (A) and the at least one sulfidic component (C) comprise the same substance, in particular selected from the group consisting of: thiodiethylene bis[3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionate], 2,2'-thiobis(6-tert-butyl-p-cresol), 4,4'-thiobis(2-tert-butyl-5-methylphenol), 4,6-bis(octylthiomethyl)-o-cresol.

In a preferred embodiment, the stabilizer system comprises the free-radical component (A), the acid component (B) and the sulfidic component (C) in an amount in each case of from 10 to 80% by weight, based on the total weight of the stabilizer system.

The stabilizer system of the invention preferably comprises

- from 10 to 80% by weight, particularly preferably from 20 to 80% by weight, of free-radical-scavenging component (A),
- from 10 to 80% by weight, particularly preferably from 10 to 50% by weight, of acid component (B) and
- from 10 to 80% by weight, particularly preferably from 10 to 50% by weight, of sulfidic component (C),

where the components add up to 100% by weight.

The stabilizer system of the invention preferably comprises

- as free-radical-scavenging component (A) one or more of the following phenols: 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione, 2,2'-methylenebis(4-ethyl-6-tert-butylphenol), pentaerythritol tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], tetrakis[methylene-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionato]]methane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, hexamethylene bis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione, alpha-tocopherol, 2,6-di-tert-butyl-4-sec-butylphenol, 2,6-di-tert-butyl-4-nonylphenol, 2,5-di-tert-amylhydroquinone, 4,4'-butylidenebis(6-tert-butyl-m cresol), 4,4',4''-(1-methylpropanyl-3-ylidene)tris[6-tert-butyl-m-cresol], 2,2'-methylenebis[6-(1-methylcyclohexyl)-p-cresol], ethylenebis(oxyethylene) bis[3-(5-tert-butyl-4-hydroxy-m-tolyl)propionate], poly(dicyclopentadiene-co-p-cresol), 6-tert-butyl-2,4-xilenol, 2,2'-(2-methylpropylidene)bis[4,6-xilenol], 2,6-di-tert-butyl-4-methylphenol, pyrogallol (1,2,3-trihydroxybenzene), propyl gallate (propyl 3,4,5-trihydroxybenzoate), C7-9-alkyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate and
- as acid component (B) one or more organic acids selected from the following group: methacrylic acid, acrylic acid and derivatives thereof, Ebecryl® 168 and Miramer® SC1400 and
- as sulfidic component (C) one or more organic sulfides selected from the group consisting of ditridecyl thiodipropionate, dilauryl thiodipropionate, distearyl thiodipropionate, dimethyl thiodipropionate, octadecyl 3-[[3-(dodecyloxy)-3-oxopropyl]thio]propionate, dimyristyl thiodipropionate, 2,2-bis{[3-(dodecylthio)-1-oxopropoxy]methyl}propane-1,3-diyl bis[3-(dodecylthio)propionate], dimercaptodiethyl sulfide dimethacrylate, 2,3-di((2-mercaptoethyl)thio)-1-propanethiol diacrylate, 2,2'-thioethanedithiol diacrylate and mixtures thereof.

The stabilizer system of the invention particularly preferably comprises

- as free-radical-scavenging component (A): 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione, pyrogallol, propyl gallate or a combination thereof,
- as acid component (B): methacrylic acid, acrylic acid, Ebecryl®168, Miramer® SC1400 or a mixture thereof and
- as sulfidic component (C): ditridecyl thiodipropionate, dilauryl thiodipropionate or a combination thereof.

The stabilizer system is used in radiation-curable or thermally curable thiol-ene and/or thiol-yne compositions, particularly preferably in a thiol-ene composition. The stabilizer system of the invention is preferably used in a radiation-curable or thermally curable thiol-ene or thiol-yne composition in an amount of from 0.05 to 1.5% by weight, particularly preferably from 0.1 to 0.5% by weight, based on the polythiol.

In addition, the invention provides a radiation-curable thiol-ene or thiol-yne composition comprising at least one stabilizer system according to the invention, at least one thiol component (D), a component comprising at least one unsaturated carbon compound (E) and a photoinitiator (F).

The thiol component (D) preferably comprises a thiol or a plurality of thiols in each case having two or more free thiol functions.

A thiol having two free thiol functions is referred to as a dithiol. In addition, thiols having two and more thiol functions are referred to as polythiols or else as polymercaptans. Esters of various mercaptocarboxylic acids and polyfunctional alcohols are commercially readily available, for example from Bruno Bock Chemische Fabrik GmbH&Co. and Evans Chemetics LP. In the case of mercaptocarboxylic acids, use is made in particular but not exclusively of thioglycolic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid and 3-mercaptobutyric acid. In the case of the esterification partners, namely the polyfunctional alcohols, use is made of ethylene glycol, trimethylolpropane, ditrimethylolpropane, pentaerythritol, dipentaerythritol and tris(2-hydroxyethyl)-1,3,5-triazinetriol and also polymeric polyols, for example based on the ethoxylated versions of the abovementioned polyols.

Apart from ester-based polythiols, it is also possible to use further polythiols which are free of ester bonds. Examples of these are dimercaptodiethyl sulfide, 2,3-bis((2-mercaptoethyl)thio)-1-propanethiol, 1,8-dimercapto-3,6-dioxaoctane (CAS 14970-87-7), and also polysulfides. Further polythiols which are free of ester bonds result, for example, from the reaction of primary and secondary amines with esters of mercaptocarboxylic acids and by reaction of epoxides with hydrogen sulfide.

The thiol component (D) preferably comprises a thiol or a plurality of thiols selected from the following group: glycol dimercaptoacetate (CAS 123-81-9), trimethylolpropane tris(2-mercaptopropionate) (CAS 10193-96-1 - 1,1,1), pentaerythritol tetramercaptoacetate (CAS 10193-99-4), glycol di(3-mercaptopropionate) (CAS 22504-50-3), trimethylolpropane tri(3-mercaptopropionate) (CAS 33007-83-9), tris[2-(3-mercaptopropionyloxy)ethyl] isocyanurate (CAS 36196-44-8), ethoxylated trimethylolpropane tri(3-mercaptopropionate) having an average

molar mass of 700 or 1300 g/mol (CAS 674786-83-5 or 345352-19-4), pentaerythritol tetra(3-mercaptopropionate) (CAS 7575-23-7), polycaprolactone tetra-3-mercaptopropionate having an average molar mass of 1350 g/mol (CAS 1622079-69-9), di-pentaerythritol hexakis(3-mercaptopropionate) (CAS 25359-71-1), pentaerythritol tetrakis(3-mercaptobutylate) (CAS 31775-89-0), polypropylene glycol 3-mercaptopropionate having an average molar mass of 800 or 2200 g/mol, which are all obtainable from Bruno Bock Chemische Fabrik and Evans Chemetics under the tradename Thiocure® with appropriate designation. In addition, the group further comprises:

Capcure ® 3-800 from the manufacturer Gabriel (CAS 72244-98-5), GABEPRO GPM 800 from the manufacturer Gabriel, POLYTHIOL™ QE-340M from the manufacturer Toray, trimercaptotriazine (CAS 638-16-4) from the manufacturer EVONIK, and the thiols sold by Bruno Bock under the names Thiocure 1200, Thiocure 1200V (Thiocure 1200 = poly[oxy(methyl-1,2-ethanediyl)], alpha-hydro-omega-hydroxy ethers with 2,2-bis(hydroxymethyl)-1,3-propanediol (4:1), 2-hydroxy-3-mercaptopropyl ethers (CAS 72244-98-5; Thiocure1200V = poly[oxy(methyl-1,2-ethanediyl)], alpha-hydro-omega-hydroxy ethers with 2,2-bis(hydroxymethyl)-1,3-propanediol (4:1), 2-hydroxy-3-mercaptopropyl ethers - CAS 72244-98-5).

The thiol component (D) is preferably selected from the group consisting of pentaerythritol tetramercaptoacetate, glycol di(3-mercaptopropionate), trimethylolpropane tri(3-mercaptopropionate), tris[2-(3-mercaptopropionyloxy)ethyl] isocyanurate, pentaerythritol tetra(3-mercaptopropionate), di-pentaerythritol hexakis(3-mercaptopropionate), pentaerythritol tetrakis(3-mercaptobutylate) or mixtures thereof. These thiols are obtainable, for example, under the tradenames Thiocure® and Evabotec® from Bruno Bock Chemische Fabrik GmbH & Co. KG or Evans Chemetics LP.

The multifunctional unsaturated organic compounds include compounds having at least one carbon double bond, known as alkenes, and/or having at least one triple bond, known as alkynes. These compounds can be pure hydrocarbons and compounds which also contain heteroatoms. Alkenes in the form of acrylates, methacrylates, allyl ethers and vinyl ethers are particularly readily available commercially and are utilized in many applications.

The unsaturated carbon compound (E) preferably comprises a multifunctional unsaturated organic compound of this type, in particular one or more acrylates, methacrylates, urethane acrylates, polyester acrylates, allyl ethers or vinyl ethers, particularly preferably an acrylate or methacrylate.

Particular preference is given to acrylates, for example trimethylolpropane triacrylate (TMPTA) (CAS 15625-89-5), butanediol diacrylate (BDDA) (CAS 1070-70-8), hexanediol diacrylate (HDDA) (CAS 13048-33-4), tripropylene glycol diacrylate (TPGDA) (CAS 42978-66-5), dipropylene glycol diacrylate (DPGDA) (CAS 57472-68-1), ethyldiglycol acrylate (EDGA) (CAS 7328-17-8),
5 methacrylates, for example trimethylolpropane trimethacrylate (e.g. Miwon MIRAMER® M3000 from the manufacturer Miwon), triallyl isocyanurate which is obtainable, for example, under the tradename TAICROS® (CAS 1025-15-6), triallyl cyanurate (TAC) (CAS 101-37-1), vinyl ethers, for example triethylene glycol divinyl ether (DVE), (CAS 765-12-8), 1,4-butanediol divinyl ether (CAS 3891-33-6), diethylene glycol divinyl ether (CAS 764-99-8) or 1,4-cyclohexanedimethanol
10 divinyl ether (CAS 17351-75-6) or allyl ethers such as allyl pentaerythritol (CAS 91648-24-7) or trimethylolpropane diallyl ether (CAS 682-09-7).

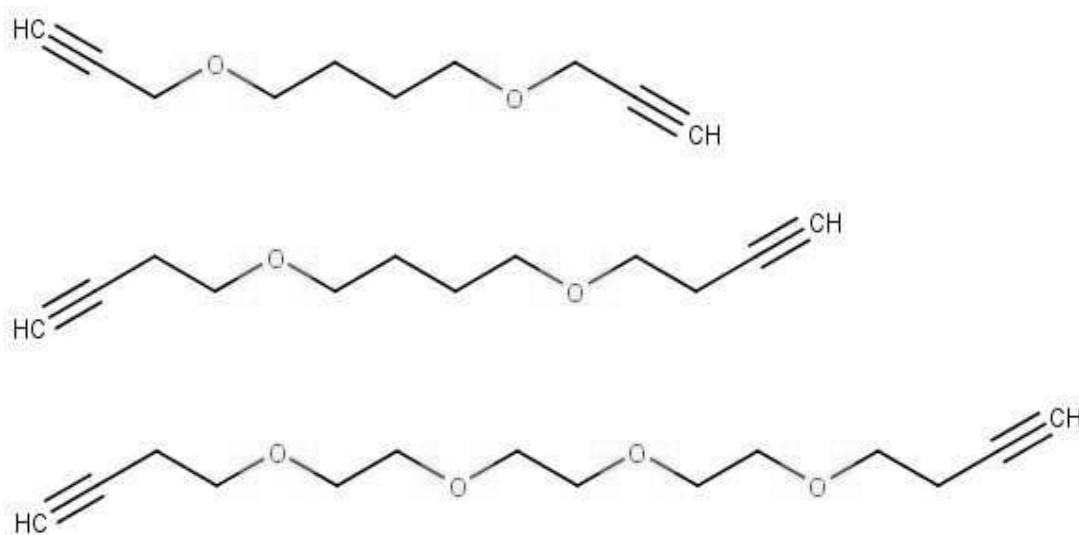
Further suitable unsaturated carbon compound (E) are diallyl pyrocarbonate, diallyl diglycol carbonate, diallyl 2,2,4-trimethylhexane-1,6-diyl dicarbamate, allyl acetate, allyl benzyl ether,
15 allyl butyl ether; allyl cyanoacetate; allyl ether; allyl ethyl ether; allyl methyl carbonate; 2-allyloxybenzaldehyde; 2-allyloxyethanol; 4-allyloxy-2-hydroxybenzophenone; 3-allyloxy-1,2-propanediol; allyl phenyl ether; monoammonium allylphosphonate; 2,2'-diallylbisphenol; 2,2'-diallyl-bisphenol A diacetate ether; diallyl carbonate; diallyl maleate; diethyl allylmalonate; 5-methyl-5-allyloxycarbonyl-1,3-dioxan-2-one; pentaerythritol allyl ether; 2,4,6-triallyloxy-1,3,5-triazine;
20 1,3,5-triallyl-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione; trimethylolpropane allyl ether; trimethylolpropane diallyl ether; 1,4-butanediol divinyl ether; 1,4-butanediol vinyl ether; butyl vinyl ether; tert-butyl vinyl ether; 2-chloroethyl vinyl ether; 1,4-cyclohexanedimethanol divinyl ether; 1,4-cyclohexanedimethanol vinyl ether; cyclohexyl vinyl ether; di(ethylene glycol) divinyl ether; di(ethylene glycol) vinyl ether; diethyl vinyl orthoformate; dodecyl vinyl ether; ethylene
25 glycol vinyl ether; 2-ethylhexyl vinyl ether; ethyl vinyl ether; isobutyl vinyl ether; phenyl vinyl ether; propyl vinyl ether; vinyl acetate; vinyl benzoate; vinyl cinnamate; vinyl decanoate; vinyl neodecanoate; vinyl neononanoate; vinyl pivalate; vinyl propionate; vinyl stearate; hexanediol divinyl ester; hexanediol divinyl carbonate; butanediol divinyl carbonate; N-vinylpyrrolidone; N-vinylcaprolactam; N-vinylimidazole; N-vinyl-N-methylacetamide; 1,4-butanediol divinyl ether;
30 diethylene glycol divinyl ether; triethylene glycol divinyl ether; 1,4-cyclohexanedimethanol divinyl ether; hydroxybutyl vinyl ether; 1,4-cyclohexanedimethanol monovinyl ether; 1,2,4-trivinylcyclohexane; diallyl (2,2,4-trimethylhexane-1,6-diyl)dicarbamate.

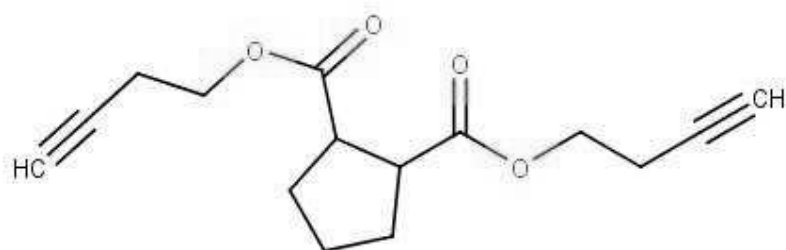
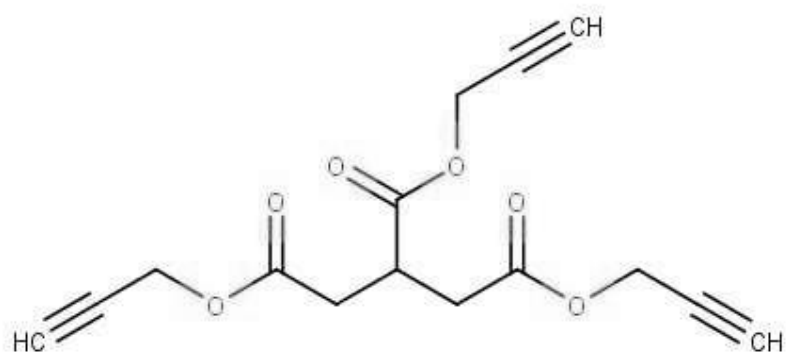
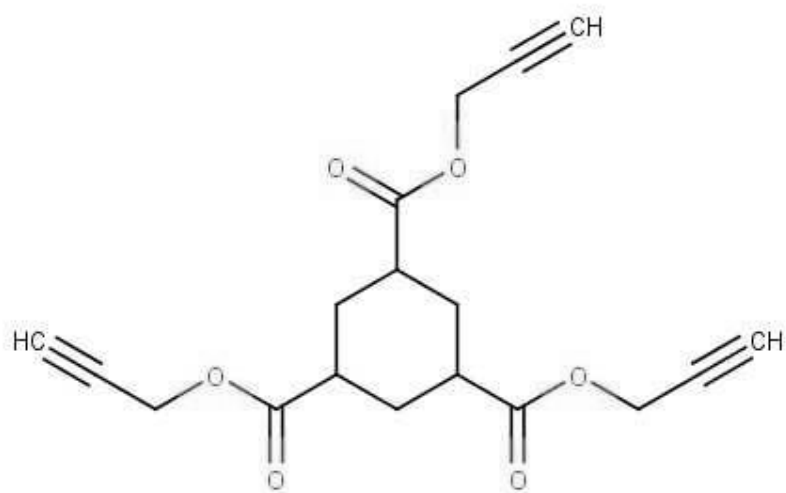
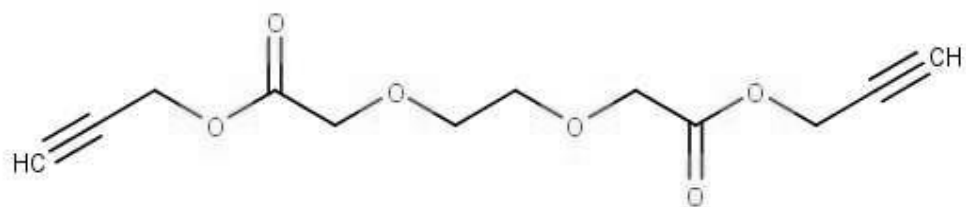
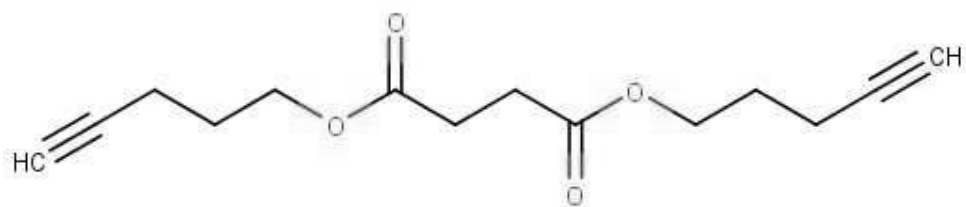
In one embodiment, the unsaturated carbon compound (E) is selected from among compounds
35 having at least one carbon-carbon double bond in a (meth)acrylic group, for example 1,4-butanediol diacrylate; 1,4-butanediol dimethacrylate; isobutyl methacrylate; 1,3-butylene glycol diacrylate; ditrimethylolpropane tetraacrylate; hexanediol diacrylate; ethoxy(3)cyclohexanoldimethanol diacrylate; 2-(2-ethoxyethoxy)ethyl acrylate; dipentaerythritol

- pentaacrylate; tripropylene glycol diacrylate; ethoxy(3)cyclohexanoldimethanol diacrylate; 2-phenoxyethyl acrylate; propoxylated (3) trimethylolpropane triacrylate; dipropylene glycol diacrylate; propoxylated (3) cyclohexanoldimethanol diacrylate; cyclic trimethylolpropane formal acrylate; ethoxylated (5) pentaerythritol tetraacrylate; ethoxy(3)hexanediol diacrylate;
- 5 ethoxy(3)phenoxyethyl acrylate; ethoxy(6)trimethylolpropane triacrylate; ethoxy(5)hexanediol diacrylate; propoxylated (6) trimethylolpropane triacrylate; propoxylated (3) hexanediol diacrylate; propoxylated (3) glyceryl triacrylate; propoxylated (2) neopentyl glycol diacrylate; 2-(2-ethoxyethoxy)ethyl acrylate; isodecyl acrylate; octyl/decyl acrylate; lauryl acrylate; tridecyl acrylate; caprolactone acrylate; diethylene glycol butyl ether acrylate; isobornyl acrylate;
- 10 tetrahydrofurfuryl acrylate; cyclic trimethylolpropane formal acrylate; isophoryl acrylate; 2-phenoxyethyl acrylate; ethoxylated (4) phenol acrylate; ethoxylated (4) nonylphenol acrylate; hexanediol diacrylate; tricyclodecanedimethanol diacrylate; dioxane glycol diacrylate; dipropylene glycol diacrylate; tripropylene glycol diacrylate; polyethylene glycol (200) diacrylate; ethoxylated bisphenol A diacrylate; propoxylated (2) neopentyl glycol diacrylate;
- 15 trimethylolpropane triacrylate; propoxylated (3) trimethylolpropane triacrylate; ethoxylated (3) trimethylolpropane triacrylate; propoxylated glycerol triacrylate; tris(2-hydroxyethyl) isocyanurate triacrylate; dipentaerythritol penta/hexaacrylate; alkoxylated pentaerythritol tetraacrylate; di(trimethylol)propane tetraacrylate; epoxy acrylate; urethane acrylate; polyester acrylate; 4-acetoxyphenethyl acrylate; 4-acryloylmorpholine; (4-benzoyl-3-hydroxyphenoxy)ethyl
- 20 acrylate; benzyl-2-propyl acrylate; butyl acrylate; tert-butyl acrylate; 2-carboxyethyl acrylate; 2-carboxyethyl acrylate; 2-chloroethyl acrylate; 2-(diethylamino)ethyl acrylate; di(ethylene glycol) ethyl ether acrylate; 2-(dimethylamino)ethyl acrylate; 3-(dimethylamino)propyl acrylate; dipentaerythritol penta/hexaacrylate; ethyl acrylate; ethyl 2-(bromomethyl)acrylate; ethyl cis(β-cyano)acrylate; ethylene glycol dicyclopentenyl ether acrylate; ethylene glycol methyl ether
- 25 acrylate; ethylene glycol phenyl ether acrylate; ethyl 2-ethylacrylate; 2-ethylhexyl acrylate; ethyl 2-propylacrylate; ethyl 2-(trimethylsilylmethyl)acrylate; hexyl acrylate; 4-hydroxybutyl acrylate; 2-hydroxyethyl acrylate; 2-hydroxy-3-phenoxypropyl acrylate; hydroxypropyl acrylate; isobornyl acrylate; isobutyl acrylate; isodecyl acrylate; isooctyl acrylate; lauryl acrylate; methyl 2-acetamidoacrylate; methyl acrylate; methyl 2-(bromomethyl)acrylate; methyl 2-
- 30 (chloromethyl)acrylate; methyl 3-hydroxy-2-methylenebutyrate; methyl 2-(trifluoromethyl)acrylate; octadecyl acrylate; pentabromobenzyl acrylate; pentabromophenyl acrylate; pentafluorophenyl acrylate; poly(ethylene glycol) diacrylate; poly(ethylene glycol) methyl ether acrylate; N-propylacrylamide; epoxidized soybean oil acrylate; tetrahydrofurfuryl acrylate; 2-tetrahydropyranyl acrylate; 3-(trimethoxysilyl)propyl acrylate; 3,5,5-trimethylhexyl
- 35 acrylate; 10-undecenylacrylate; urethane acrylate methacrylate; allyl methacrylate; 2-[3-(2H-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate; benzyl methacrylate; bis(2-methacryloyl)oxyethyl disulfide; butyl methacrylate, tert-butyl methacrylate, 9H-carbazole-9-ethyl methacrylate; cyclohexyl methacrylate; 1,10-decamethylene glycol dimethacrylate; 2,5-

- (diethylamino)ethyl methacrylate; diethylene glycol butyl ether methacrylate; di(ethylene glycol) methyl ether methacrylate; 2-(diisopropylamino)ethyl methacrylate; 2-(dimethylamino)ethyl methacrylate; 2-ethoxyethyl methacrylate; ethylene glycol dimethacrylate; ethylene glycol dicyclopentenyl ether methacrylate; ethylene glycol methyl ether methacrylate; ethylene glycol phenyl ether methacrylate; 2-ethylhexyl methacrylate; ethyl methacrylate; furfuryl methacrylate; glycidyl methacrylate; glycosyloxyethyl methacrylate; hexyl methacrylate; hydroxybutyl methacrylate, 2-hydroxyethyl methacrylate; 2-hydroxyethyl methacrylate; hydroxypropyl methacrylate; 2-hydroxypropyl-2-(methacryloyloxy)ethyl phthalate; 2-hydroxy-3-{3-[2,4,6,8-tetramethyl-4,6,8-tris(propyl glycidyl ether)-2-cyclotetrasiloxanyl]propoxy}propyl methacrylate; isobornyl methacrylate; isobutyl methacrylate; 2-isocyanatoethyl methacrylate; isodecyl methacrylate; lauryl methacrylate; methyl methacrylate; 2-(methylthio)ethyl methacrylate; mono-2-(methacryloyloxy)ethyl maleate; mono-2-(methacryloyloxy)ethyl succinate; 2-N-morpholinoethyl methacrylate; 1-naphthyl methacrylate; 1,4-phenylene dimethacrylate, phenyl methacrylate; phosphoric acid 2-hydroxyethyl methacrylate ester; 1-pyrenemethyl methacrylate; pyromellitic dianhydride dimethacrylate; tetraethylene glycol dimethacrylate; tetrahydrofurfuryl methacrylate; triethylene glycol dimethacrylate; triethylene glycol methyl ether methacrylate; 3,3,5-trimethylcyclohexyl methacrylate, urethane acrylate methacrylate; urethane epoxymethacrylate; vinyl methacrylate; and urethane dimethacrylate.
- 20 In one embodiment, the unsaturated compound (E) is a compound having at least one carbon triple bond, known as an alkyne. Suitable alkyne compounds are, for example, unsaturated compounds (E) having at least one terminal functional alkyne groups or more terminal functional alkyne groups. By way of example, it is possible to use the following alkynes:

25





Further suitable compounds are di(but-3-yn-1-yl) carbonate, di(prop-2-yn-1-yl) carbonate and di(but-3-yn-1-yl) 2,2,4-trimethylhexane-1,6-diyl dicarbamate.

5

The unsaturated compound (E) is preferably selected from the group consisting of an acrylate selected from among TMPTA (trimethylolpropane triacrylate), PETTA (pentaerythritol tetraacrylate), DPHA (dipentaerythritol hexaacrylate), a methacrylate selected from among EGDMA - ethylene glycol dimethacrylate and TMPTMA – trimethylolpropane trimethacrylate or

10 triallyl isocyanurate, allylpentaerythritol or trimethylolpropane diallyl ether or a combination of the monomers mentioned.

The photoinitiator (F) is preferably selected from the group consisting of: 2-hydroxy-2-methyl-1-phenylpropan-1-one (CAS 7473-98-5), bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (CAS

15 162881-26-7), phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide, 2,2-dimethoxy-1,2-diphenylethan-1-one, 2,4,6-trimethylbenzoyldiphenylphosphine oxide (CAS 75980-60-8), 2,4,6-trimethylbenzoylthoxyphenylphosphine oxide (CAS 84434-11-7) and mixtures thereof.

The thiol-ene composition of the invention preferably contains at least one thiol component (D)

20 selected from the group consisting of pentaerythritol tetramercaptoacetate, tris[2-(3-mercaptopropionyloxy)ethyl] isocyanurate and pentaerythritol tetra(3-mercaptopropionate) or mixtures thereof, and a component comprising at least one unsaturated carbon compound (E) selected from the group consisting of trimethylolpropane triacrylate, pentaerythritol tetraacrylate, dipentaerythritol hexaacrylate, ethylene glycol dimethacrylate, trimethylolpropane

25 trimethacrylate, triallyl isocyanurate, allylpentaerythritol and trimethylolpropane diallyl ether.

As stabilizer system, the radiation-curable thiol-ene or thiol-yne composition of the invention preferably comprises 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione, pyrogallol, propyl gallate or a combination thereof as free-radical-scavenging

30 component (A), methacrylic acid, acrylic acid, Ebecryl®168 or a mixture thereof as acid component (C) and ditridecyl thiodipropionate, dilauryl thiodipropionate, dimethyl thiodipropionate or a combination thereof as sulfidic component (C).

In a preferred embodiment, the radiation-curable thiol-ene or thiol-yne composition comprises

35 the inventive stabilizer system in an amount of from 0.05 to 1.5% by weight, more preferably from 0.1 to 0.5% by weight, particularly preferably from 0.1 to 0.25% by weight, based on the polythiol.

The stabilizer system of the invention prevents undesirable reactions in the thiol-ene or thiol-yne composition according to the invention during storage, so that relatively long storage without an effect on quality is possible. An increase in the viscosity, which indicates undesirable commencement of the reaction, does not occur and a doubling of the viscosity, which is an indicator of this, can be effectively prevented. Gelling of the sample is prevented. The stabilizer system of the invention does not, however, lead to a desired reaction of the thiol with alkenes or alkynes in the respective thiol-ene and thiol-yne composition no longer being possible or no longer being possible at a satisfactory rate. A thiol-ene or thiol-yne composition which has been admixed with the stabilizer system of the invention displays sufficient reactivity despite the stabilizer system and can be cured normally.

Further features, details and advantages of the invention may be derived from the wording of the claims and also from the following description of working examples.

15 Description of the methods:

Production of the samples:

Mixing of the individual components with the exception of the photoinitiator and the unsaturated compound was carried out, after weighing out on an analytic balance, by stirring on a laboratory magnetic stirrer. The stirring time was from 30 to 120 minutes. To assist solubility, it was sometimes necessary here to increase the temperature of the mixture to up to 50°C.

The unsaturated component and the photoinitiator were firstly mixed separately. The mixing process was carried out in a planetary centrifugal mixer (model: Thinky ARE-250). The stirring time was 90 seconds at a speed of 2000 revolutions per minute.

The two mixtures were likewise mixed in a planetary centrifugal mixer for 90 seconds at a speed of 2000 revolutions per minute and then degassed for 30 seconds at 2200 revolutions per minute.

30

Determination of the viscosity:

A Haake Viscotester iQ from Thermo Fisher was used for determining the viscosity. A combination of the rotor C352°/Ti under plate TMP35 was employed. The measurement was carried out with regulation of the temperature at 20°C. The measured values are reported in mPas.

35

Storage of the samples:

Storage of the samples was carried out at room temperature and at 60°C in a convection drying oven.

As soon as doubling of the viscosity of a thiol-ene or thiol-yne composition had occurred, this composition was considered to be unusable for the application. In view of this, the measurements of the viscosity of the respective sample were usually stopped as soon as a doubling of the viscosity was observed.

The invention is illustrated with the aid of the following examples:

10

Thiol-ene compositions having the formulations indicated in Table 1 and Table 2 were produced:

	C1	C2	C3	C4
Triallyl isocyanurate (TAICROS®)	39.7 g	39.7 g	39.7 g	39.7 g
Pentaerythritol tetra(3-mercaptopropionate)	60.3 g	60.3 g	60.3 g	60.3 g
2,4,6-Trimethylbenzoyl ethoxyphenylphosphine oxide	0.5 g	0.5 g	0.5 g	0.5 g
Pyrogallol	- -	0.05 g	- -	- -
Ditridecyl thiodipropionate	- -	- -	0.1 g	- -
Ebercyl ® 168	- -	- -	- -	0.1 g

Table 1: Formulations of the thiol-ene compositions of Comparative Examples C1, C2, C3 and C4

15

Abbreviations: free-radical-scavenging component (A)
acid component (B)
sulfidic component (C)

C1: without stabilizer system, i.e. without components (A), (B) and (C)

C2: with pyrogallol as free-radical-scavenging component (A), components (B) and (C) not added

C3: with ditridecyl thiodipropionate as sulfidic component (C), components (A) and (B) not added

C4: with Ebercyl ® 168 (acidic methacrylate) as acid component (B), components (A) and (C) not added

20

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	1	2	3
Triallyl isocyanurate (TAICROS®)	39.7 g	39.7 g	39.7 g
Pentaerythritol tetra(3-mercaptopropionate)	60.3 g	60.3 g	60.3 g

2,4,6-Trimethylbenzoylthioethoxyphenylphosphine oxide	0.5 g	0.5 g	0.5 g
Pyrogallol	0.05 g	0.05 g	0.05 g
Ditridecyl thiodipropionate	0.05 g	0.05 g	0.05 g
Ebercyl ® 168	0.05 g	--	--
Acrylic acid	--	0.05 g	--
Methacrylic acid	--	--	0.05 g

Table 2: Formulations of thiol-ene compositions according to the invention as per Examples 1, 2, 3

The thiol-ene components produced were stored as described above. After defined storage times, the viscosity was measured. An increase in viscosity indicates that the thiol-ene reaction has commenced and the composition is no longer storage-stable. The sample gels and could thus not be used and applied. The values from the viscosity measurements are reported in Tables 3, 4, 5 and 6. The viscosity is reported in mPas. The measurement was carried out using the above-described methods.

Measurement	C1	1	2	3
	(D+E+F) without stabilizer	(D+E+F) + (A+B+C)	(D+E+F) + (A+B+C)	(D+E+F) + (A+B+C)
Initially	515	506	497	479
After 1 day		525	540	528
After 6 days	541			
After 8 days		518	524	533
After 8 weeks		506	453	502
After 3 months		492	508	503

Table 3: Results of the viscosity measurements on the samples C1 and 1 to 3 at 20°C;
Viscosity in mPas

Abbreviations: Thiol component (D)

Component with unsaturated carbon compound (E)

Photoinitiator (F).

Measurement	C2	C3	C4
	(D+E+F) + A	(D+E+F) + B	(D+E+F) + C
Initially	542	548	523
After 1 day	524	527	522

After 10 days	510	576	533
After 20 days	486	599	536
After 11 weeks	421	902	787
After 15 weeks	540	1413	1758

Table 4: Results of the viscosity measurements on the samples C2 to C4 at 20°C;
viscosity in mPas

Abbreviations: free-radical-scavenging component (A)

acid component (B)

sulfidic component (C)

5

Measurement	C1	1	2	3
	(D+E+F) without stabilizer	(D+E+F) + (A+B+C)	(D+E+F) + (A+B+C)	(D+E+F) + (A+B+C)
Initially	515	506	497	479
After 1 day	1889	526	544	537
After 6 days	7695			
After 8 days		611	625	603
After 8 weeks		1249	1413	1381

Table 5: Results of the viscosity measurements on the samples C1 and 1 to 3 at 60°C,
viscosity in mPas

Measurement	C2	C3	C4
	(D+E+F) + A	(D+E+F) + B	(D+E+F) + C
Initially	542	548	523
After 1 day	538	1138	871
After 10 days	689	3970	2768
After 20 days	737		
After 11 weeks	1589		

Table 6: Results of the viscosity measurements on the samples C2 to C4 at 60°C,
viscosity in mPas

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	C5	C6	4
Trimethylolpropane triacrylate (TMPTA)	44.0 g	44.0 g	44.0 g
Pentaerythritol tetra(3-mercaptopropionate)	56.0 g	56.0 g	56.0 g

2,4,6-Trimethylbenzoylthioethoxyphenylphosphine oxide	0.5 g	0.5 g	0.5 g
Pyrogallol	- -	0.05 g	0.05 g
Ditridecyl thiodipropionate	- -	- -	0.05 g
Ebercryn® 168	- -	- -	0.05 g

Table 7: Formulations of the thiol-ene composition according to the invention as per Example 4 and the Comparative Examples C5 and C6

C5 Stabilizer system with components (A), (B) and (C) not added

C6 Pyrogallol as free-radical-scavenging component (A), components (B) and (C) not added

5

Measurement	C5 (20°C)	C5 (60°C)	C6 (20°C)	C6 (60°C)	B4 (20°C)	B4 (60°C)
	(D+E+F) without stabilizer	(D+E+F) without stabilizer	(D+E+F) + A	(D+E+F) + A	(D+E+F) + (A+B+C)	(D+E+F) + (A+B+C)
Initially	461	461	300	300	301	301
After 1 day	925	10 000			319	311
After 10 days			289	335	307	345
After 20 days			327	439	296	376
After 9 weeks			288	678	294	410
After 12 weeks			297	885	294	681
After 15 weeks			270		276	

Table 8: Results of the viscosity measurements on the samples C5, C6 and B4 at 20°C and 60°C;

Viscosity in mPas. The measurement was carried out using the above-described methods.

10

The results of the viscosity measurements from Table 8 are also depicted in Fig. 1. It can be seen that without the stabilizer system, a sharp increase in viscosity commences immediately after commencement of storage (C5). The viscosity increase can be slowed somewhat by addition of a free-radical-scavenging component, but significantly better stabilization can be achieved by the synergistic effect of the stabilizer system composed of free-radical-scavenging component (A), acid component (B) and sulfidic component (C) without impairing the desired reactivity.

15

The examples show that thiol-ene composition without the stabilizer system of the invention have only a low storage stability. Particularly at an elevated temperature of 60°C, a viscosity increase can be measured on the composition without the stabilizer system according to the invention after only 6 days (C1) or only 10 days (C3 and C4).

5

The invention is not limited to one of the above-described embodiments, but can be modified in a variety of ways.

10 All features and advantages indicated in the claims and the description, including structural details, spatial arrangements and process steps, can be essential to the invention both in themselves and also in a variety of combinations.

Patent Claims

- 5 1. Stabilizer system, in particular for thiol-ene and/or thiol-yne compositions, comprising the following components:
- at least one free-radical-scavenging component (A),
 - at least one acid component (B), where the acid component (B) comprises one or more organic acids, and
 - 10 - at least one sulfidic component (C) selected from the group consisting of organic sulfides.
2. Stabilizer system according to Claim 1, **characterized in that** the free-radical-scavenging component (A) comprises one or more free-radical scavengers selected from
- 15 the following group: sterically hindered phenols, sterically hindered naphthalenes and sterically hindered amines.
3. Stabilizer system according to either of the preceding claims, **characterized in that** the free-radical-scavenging component (A) comprises pyrogallol, 1,3,5-tris(4-tert-butyl-3-
- 20 hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione, propyl gallate or a combination thereof.
4. Stabilizer system according to any of the preceding claims, **characterized in that** one or more organic acids of the acid component (B) have a pKa in the range from 1 to 5.5 at
- 25 25°C.
5. Stabilizer system according to any of the preceding claims, **characterized in that** the acid component (B) comprises one or more unsaturated carboxylic acids, in particular selected from the following group: methacrylic acid, acrylic acid, and derivatives thereof.
- 30 6. Stabilizer system according to any of the preceding claims, **characterized in that** the sulfidic component (C) comprises one or more organic sulfides selected from the following group: ditridecyl thiodipropionate, dilauryl thiodipropionate, distearyl thiodipropionate, dimethyl thiodipropionate, octadecyl 3-[[3-(dodecyloxy)-3-
- 35 oxopropyl]thio]propionate, dimyristyl thiodipropionate.
7. Stabilizer system according to any of the preceding claims, **characterized in that** the at least one free-radical-scavenging component (A) and the at least one sulfidic component

(C) comprise the same substance, in particular selected from the group consisting of: thiodiethylene bis[3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionate], 2,2'-thiobis(6-tert-butyl-p-cresol), 4,4'-thiobis(2-tert-butyl-5-methylphenol), 4,6-bis(octylthiomethyl)-o-cresol.

- 5 8. Stabilizer system according to any of the preceding claims, characterized in that the free-radical-scavenging component (A) is used in an amount of from 10 to 80% by weight and the acid component (B) and the sulfidic component (C) are each used in an amount of from 10 to 50% by weight, based on the stabilizer system.
- 10 9. Use of a stabilizer systems according to any of the preceding claims for a radiation-curable or thermally curable thiol-ene and/or thiol-yne composition comprising at least one thiol component (D) in combination with at least one unsaturated carbon compound (E).
- 15 10. Radiation-curable thiol-ene or thiol-yne composition comprising at least one stabilizer system according to any of Claims 1 to 8, at least one thiol component (D), a component comprising at least one unsaturated carbon compound (E) and a photoinitiator (F).
- 20 11. Radiation-curable thiol-ene or thiol-yne composition according to Claim 10,
characterized in that the thiol component (D) comprises a thiol or a plurality of thiols each having two or more free thiol functions.
- 25 12. Radiation-curable thiol-ene or thiol-yne composition according to Claim 10 or 11,
characterized in that the stabilizer system is present in an amount of from 0.05 to 1.5% by weight, in particular from 0.1 to 0.25% by weight, based on the polythiol.