

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
22 January 2009 (22.01.2009)

PCT

(10) International Publication Number
WO 2009/010423 A1

(51) International Patent Classification:

C09D 181/04 (2006.01) **C03C 27/12** (2006.01)
B32B 17/10 (2006.01) **C08G 75/04** (2006.01)

(21) International Application Number:

PCT/EP2008/058856

(22) International Filing Date: 8 July 2008 (08.07.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/959,802 17 July 2007 (17.07.2007) US

(71) Applicant (for all designated States except US): **CYTEC SURFACE SPECIALTIES, S.A.** [BE/BE]; Square Marie Curie 11, B-1070 Brussels (BE).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **MILLER, Christopher Wayne** [US/US]; 1186, Norfolk Drive NW, Acworth, Georgia 30102 (US). **SHAW, Jonathan** [US/US]; 5580 Hedge Brooke Drive, Acworth, Georgia 30101 (US).

(74) Agent: **DESTRYKER, Elise**; Cytec Surface Specialties, S.A., Anderlechtstraat 33, B-1620 Drogenbos (BE).

(81) Designated States (unless otherwise indicated, for every

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

(84) Designated States (unless otherwise indicated, for every

kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

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

(54) Title: MULTICOMPONENT THIOL-ENE COMPOSITIONS FOR LAMINATE MATERIALS

(57) Abstract: The present invention is directed to a laminate composition, comprising (1) one or more thiol-functional compounds; (2) one or more oligomeric or polymeric compounds containing one or more carbon-carbon double bonds or triple bonds; and (3) one or more monomeric compounds containing one or more carbon-carbon double bonds or triple bonds. The present invention is also directed to methods of producing glass and/or polymer laminates using the above composition, glass and/or polymer laminates made from the method, and machines or articles of manufacture incorporating the above laminates.



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MULTICOMPONENT THIOL-ENE COMPOSITIONS FOR LAMINATE MATERIALS

BACKGROUND OF THE INVENTION

5 1. Field of the Invention

This invention relates to the use of thiol-ene based radiation curable formulations for laminate applications. More specifically, this invention relates to the use of binary, ternary, and/or multi-component chemical systems comprising thiol-enes as radiation-curable formulations. The thiol-ene comprising formulations are suitable for use as the polymeric
10 interlayers for glass laminate applications including, but not limited to, typical applications such as hurricane windows, doors, and curtainwalls; acoustical dampening windows, doors and curtainwalls; ballistic resistant glass, and safety glass.

15 2. Brief Description of the Related Art

The technique of laminating glass panes, i.e. binding two or more glass panes together in a permanent way by an interlayer, is well known and generally applied. Such glass laminates are used for example in automotive and building applications.

In the present description, the term "glass" is used to designate objects made of glass or of glass appearance. Glass appearance objects such as polycarbonate panels can be used but are
20 less preferred because of their poor behavior in case of fire. The glass objects can be made of ordinary float glass, whether heat treated or not, or of special glass such as borosilicate glass.

Laminating protects people from splinters in case of glass breaking, and it also provides additional properties to the glazing. Basically, laminated glass is industrially produced either by a polymer film system, or by liquid cast-in-place resin polymerized in situ.

25 The film lamination technology often comprises the insertion of an organic, polymeric film between two glass panes, and bonding them at an elevated temperature under an elevated pressure. Different materials can be used, for example polyvinylbutyral (PVB) as the organic film. The foil is positioned on a glass pane, and a second pane positioned upon the film. The so-formed sandwich has to be passed through an oven, to weaken the film and create a preliminary
30 adhesion. The sandwich then undergoes a batch-wise heating and pressure cycle, in order to bring the film in close contact with the glass and to develop adhesion onto the glass surfaces.

This operation is done in an autoclave, at 120 to 150°C and with increased pressure, typically between 10 to 17 kg/cm³, in order to bring the film in close contact with the glass and to develop adhesion onto the glass surfaces. Residence time in the autoclave at the required temperature is 30 to 45 minutes, longer for bent or multiple laminates. The total residence time, including heating and subsequent cooling is about 2 hours. The PVB film lamination process is described in ‘Encyclopedia of Chemical Technology’ – KIRK-OTTMER – 4th edition, Volume 14, page 1059 – 1074. The main restrictions to this system are the high investment costs, while also the size of the autoclave can be restrictive in the case of larger panels and bent glazing. Moreover, the film lamination is a batch-wise process and requires a high-energy input. A large size apparatus is required, and the total operation time is long. Also, it is more difficult to apply on certain glass surfaces, e.g. toughened glass that is not completely flat. In such situations, the film is not elastic enough to adapt to the uneven surface. Also for bent glass it is more difficult to apply, when the curving of both glass panes would not be identical.

A possible solution to compensate for glass surface unevenness is to apply more film layers, 4 or 6 or more layers instead of the 1 or 2 layers as typically used. However, in this way significantly more organic combustible material is incorporated.

An alternative lamination technique is by the use of liquid resin, cured in situ.

Two glass panes are bound together by a double-sided adhesive tape that also functions as a spacer. The cavity between the two sheets is then filled up with a liquid resin. Typically the envelope is positioned at an angle of at least 60° during filling. After complete filling, the filled sandwich is slowly returned to horizontal, allowing the liquid to flow throughout the entire cavity. When the liquid reaches the filling opening, the opening is sealed with hot melt material. Any entrapped air is then removed with a small syringe. The liquid resin is then polymerized, the so-called “curing” step. Curing can be accomplished either by radiation, or chemically by appropriate catalysts and accelerators.

Polymerization, the so-called “curing” step, chemically changes the liquid resin into a solid polymeric interlayer. There is basically no visual differentiation between foil laminated glazing and resin laminated glazing. The equipment needed for resin lamination may be as little as one or two tilting tables to allow the assembly of the envelope, a dosing pump and, in case of radiation cure, a radiation source. A strong technical advantage of the liquid resin system is that the cavity between the two glasses is completely filled up with the liquid resin, thus the influence

of the shape or roughness of the glass surfaces on the bonding with the resin interlayer is significantly reduced. The incorporation of adhesion promoters(s), most often appropriate silanes, allows for a chemical bond to be created between the silanol (- Si - OH) functions on the glass surface, and the interlayer. A chemical bond is stronger than simple physical adhesion, and
5 is typically more stable over time.

The chemical nature of the liquid resins used for glass lamination can be of different kinds, for example polyester, polyurethane, silicone or, most often, acrylic. The latter is preferred for its high resistance against outdoor weathering conditions, i.e. UV radiation, heat and humidity.

10 An example of a polyester-based liquid resin system, for manufacturing acoustic glazing, is described in French patent 1367977, "Acoustic Laminates", by Saint-Gobain Industries of France. An example of a urethane acrylate-based liquid resin system, for manufacturing clear glazing, is given in EP0108631, by DeltaGlass S.A.

Curing of the liquid resin can be initiated directly by inclusion of one or more catalysts,
15 accelerants, or highly reactive components in the liquid resin mixture, or indirectly by heating, irradiation with UV or visible electromagnetic radiation, or exposure to electron-beam radiation. For direct chemical initiation one or more catalysts and an accelerator are added to the base resin, this is the so-called multi-component system. Each of the above mentioned chemical types of resins could be multi-component.

20 The reaction starts after the blending of the catalyst(s) and the accelerator with the resin, after a period of time that depends on the resin composition, the concentrations of catalyst(s) and accelerator, and the temperature of the substrates and the environment.

Additionally, IR radiation sources can be applied to increase reaction speed.

Polymerization of radiation curable resins is initiated by irradiation of photosensitive
25 components in the resin formulation with electromagnetic radiation typically in the ultraviolet and/or visible spectral regions, or by exposure of the resin to electron beam radiation. Most typically, in the case of radiation cure, the radiation source comprises one or more fluorescent bulbs, arc lamps, light emitting diodes (LEDs), or microwave lamps in an assembly that when energized irradiates the filled laminate with electromagnetic radiation primarily in the ultraviolet
30 and visible spectral range. In some cases, the radiation source comprises a device that irradiates the filled laminate with a beam of electrons to initiate polymerization.

UV curable liquid resin systems are described in i.e. EP0108631.

Most often UV resins for glass laminates are initiated by the action of UV light of low intensity with an exposure time of typically 15 to 30 minutes.

Different chemical types of polymer precursors are possible, while most commonly, ethylenically unsaturated resins based upon esters of (meth)acrylic acid and derivatives thereof containing polyester, urethane, or polyether functionality are used.

(Meth)acrylate-based UV curable polymer precursors for glass laminates typically contain:

- a reactive oligomer, i.e. a (meth)acrylated urethane oligomer,
- 10 - reactive diluents, i.e. (meth)acrylated monomers,
- the monomers can be one or more of the following: 2-ethylhexyl acrylate, 1,6-hexanediol diacrylate, n-hexyl acrylate, n-hexyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, isobornyl acrylate, isobornyl methacrylate, isooctyl acrylate, n-lauryl acrylate, n-lauryl methacrylate, methyl methacrylate (MAM), butyl acrylate, acrylic acid,
- 15 methacrylic acid, isobutyl acrylate, cyclohexyl acrylate, 2-butoxyethyl acrylate, cyclohexyl acrylate, N-vinyl pyrrolidone, and the like, with the preferred ones in the field of glass laminates being mono-functional monomers that are low in viscosity and provide a relatively higher glass transition temperature in the cured interlayer,
- one or more photo-initiators,
- 20 - adhesion promoters, for example silane compounds
- additives, for example stabilizers.

Laminated glass is used in the automotive and the building industry. Its functions can be manifold, although typically the main objectives are sound insulation and safety and security performance.

25 Glazing in the building industry has several functions, more or less dependent on its application:

- regulation of the incident light with respect to clarity and transparency, control of the heat transmission from infrared solar irradiation,
- physical integrity, protection against wind and heat,
- 30 - heat insulation,
- acoustic insulation,

- safety and/or security performances, to protect people against falling through glazing and against falling glass, to protect against burglary and vandalism,

- fire resistance

- bomb blast resistance

5 - decoration.

Traditional film or resin laminated glass fulfils most of these functions, in particular film or resin laminated glass may have very good properties as to sound reduction and impact resistance.

As mentioned above, in laminate applications, multi-component formulations are pre-
10 mixed or mixed in-situ and injected into a gap between glazing layers (lites) (preferably glass to glass, but can be glass to polymer, or polymer to polymer, etc.), and subsequently polymerized through irradiation (preferably UV-A type irradiation) to form a polymeric interlayer between the lites of glass (or polymer). The polymerized interlayer serves to adhere one lite to the other and also serves to dissipate energy under high shear (i.e. from ballistic impact), while also
15 providing rigidity under low shear deformation (e.g. window pressure cycling) of the laminate structure. Additionally, due to excellent adhesion to the lites, the interlayer prevents release of dangerously small and ballistic shards of glass (or polymer) upon impact of a projectile or other breakage of the glass.

For hurricane window applications, achieving an optimal balance of high shear energy
20 dissipation to prevent interlayer penetration during ballistic impacts, in combination with sufficient low-shear rigidity to prevent flex-related pullout from the frame during pressure cycling has proven to be very difficult for large window sizes using the conventional radiation-curable (meth)acrylate chemistry. This dichotomous application need which requires flexibility to improve high shear energy dissipation, and yet requires rigidity to minimize flex under low-
25 shear large-area pressure-induced deformation and to achieve sufficient toughness to prevent interlayer penetration is a difficult challenge. Thus, known radiation curable glass laminate interlayers, such as UVEKOL[®]-S, are not capable of meeting the performance requirements for large hurricane windows or certain corner window applications where relatively higher pressure cycles may occur. Competitive polymer ionomer-based materials such as Dupont SentryGlas[®]
30 Plus are available that meet the performance needs, but via a less advantageous window manufacturing process and at a much higher cost.

New formulations of curable formulations for laminate applications are therefore desired, and this invention is believed to meet those needs by providing a tough, polymeric interlayer that is sufficiently flexible to dissipate energy from ballistic impact while also providing sufficient rigidity to minimize laminate flex under large-area pressure deformations, and embodied in a technology and manufacturing process that provides the advantages of the liquid-fill in-situ polymerized laminate systems.

SUMMARY OF THE INVENTION

In one aspect, the present invention is directed to a laminate composition, comprising (1) one or more thiol-functional compounds; (2) one or more oligomeric or polymeric compounds containing one or more carbon-carbon double bonds or triple bonds; and (3) one or more monomeric compounds containing one or more carbon-carbon double bonds or triple bonds.

In another aspect, the present invention is directed to a method of producing a glass laminate, comprising the steps of (1) providing at least two juxtaposed panes of glass and/or polymer having a gap between them; (2) applying the above laminate composition into the gap; and (3) curing the composition.

In another aspect, the present invention is directed to a glass laminate comprising at least two juxtaposed panes of glass having a gap between them, the gap filled with the above composition in a cured state.

In additional aspects, the present invention is also directed to methods of producing glass and/or polymer laminates using the above composition, glass and/or polymer laminates made from the method, and machines or articles of manufacture incorporating the above laminates.

These and other aspects will become apparent upon reading the following detailed description of the invention.

DETAILED DESCRIPTION OF THE INVENTION

Use of UVEKOL[®] type radiation-curable materials for manufacturing laminated glass windows offers many advantages including a fast curing process that is not temperature dependent, a one-component product that requires no mixing, and solvent-free materials that facilitate easy disposal and clean-up. However, certain parameters of these systems are less

advantageous. For example, viscoelastic properties, impact dissipation properties, and rigidity of the formed products are not always suitable for certain applications.

The inventors have unexpectedly found that the compositions of the present invention overcome these limitations. Specific advantages of thiol-ene component chemical systems disclosed in the present invention include tailored viscoelastic properties of the cured interlayer that may provide for a significantly higher level of energy absorption and dissipation by the interlayer under ballistic impact as well as tailored rigidity under low-shear deformation of the laminate. This chemistry demonstrates a step-change in performance relative to the existing UVEKOL[®]-type formulations. When properly formulated, the thiol-ene formulations of the present invention also provide advantages for reduced photodegradation, reduced handling hazards relative to the commercial (meth)acrylate formulations, improved cure times, resistance to oxygen inhibition, and capability for curing very thick segments.

The technical basis of this step-change in application performance is tailoring of the rheological characteristics of the cured interlayer, for example by manipulation of the temperature and width of the glass transition temperature of the polymer interlayer through morphological design. The morphological design is achieved by intelligent selection of thiol component as well as one or more types of "ene" components, wherein variables are optimized including: (1) reactivity ratios of the enes for radical copolymerization relative to homopolymerization relative to Michael addition relative to thiol-ene step-growth polymerization (2) structural features of the "ene" such as aromaticity, flexibility, molecular weight, ene functionality (i.e. (meth)acrylate, vinyl ether, alkene, urethane, polyester, polyether, etc.), linear, branched, dendritic, etc. (3) structural features of the thiol such as thiol functionality, molecular weight, flexibility, etc. (4) kinetic rate effects through quantity and type(s) of photoinitiator(s).

Intelligent manipulation of these compositional and process-related variables in thiol-ene multicomponent systems permits formation of novel morphologies such as interpenetrating polymer networks, tough materials with a very narrow or specific temperature T_g , durable highly elastic networks, durable inelastic networks, etc. These morphologies and resulting polymer viscoelastic properties are due the nature of the components and to the different reactions that may occur during the polymerization of the mixture: (1) thiol-ene polymerization through Michael addition (2) thiol-ene polymerization through step-growth chain mechanism (3)

homopolymerization of the ene components (4) copolymerization of the ene components (5) cross polymerization of thiol-ene segments with free-radical homopolymers or copolymers of the ene components through chain-transfer and other reactions, as well as to secondary interactions within the resulting polymer structure such as (6) hydrogen bonding (7) pi-stacking (8) ionic
 5 interactions (9) dipolar interactions, and the like.

As indicated above, the present invention is directed to a laminate composition, comprising: (1) one or more thiol-functional compounds, (2) one or more oligomeric or polymeric compounds containing one or more carbon-carbon double bonds or triple bonds (the “ene” component); and (3) one or more monomeric compounds containing or more carbon-
 10 carbon double bonds or triple bonds. Each of these components is discussed in more detail below.

The thiol-functional component of the invention may be any poly-thiol functional molecule, oligomer, or polymer. Thiol functionality of 3 or more thiol groups per molecule is preferred. More than one thiol functional compound may be used in any particular formulation
 15 of this invention. Examples of preferred thiols are shown in Table 1 and Figure 1.

Table 1. Examples of Thiol-Functional Compounds

NAME	TYPE	Functionality
Pentaerythritol tetrakis(3-mercaptopropionate)	thiol	4
Trimethylopropane tris(3-mercaptopropionate)	thiol	3
TMXDI tetra thiol	thiol	4
IPDI tetra thiol	thiol	4
HDI tetra thiol	thiol	4
Hexanedithiol	thiol	2
Ethyleneglycol di-2-mercaptoacetate	thiol	2
Pentaerythritol tetrakis(2-mercaptoacetate)	thiol	4
Trimethylopropane tris(2-mercaptoacetate)	thiol	3
Ethyleneglycol di-3-mercaptopropionate	thiol	2

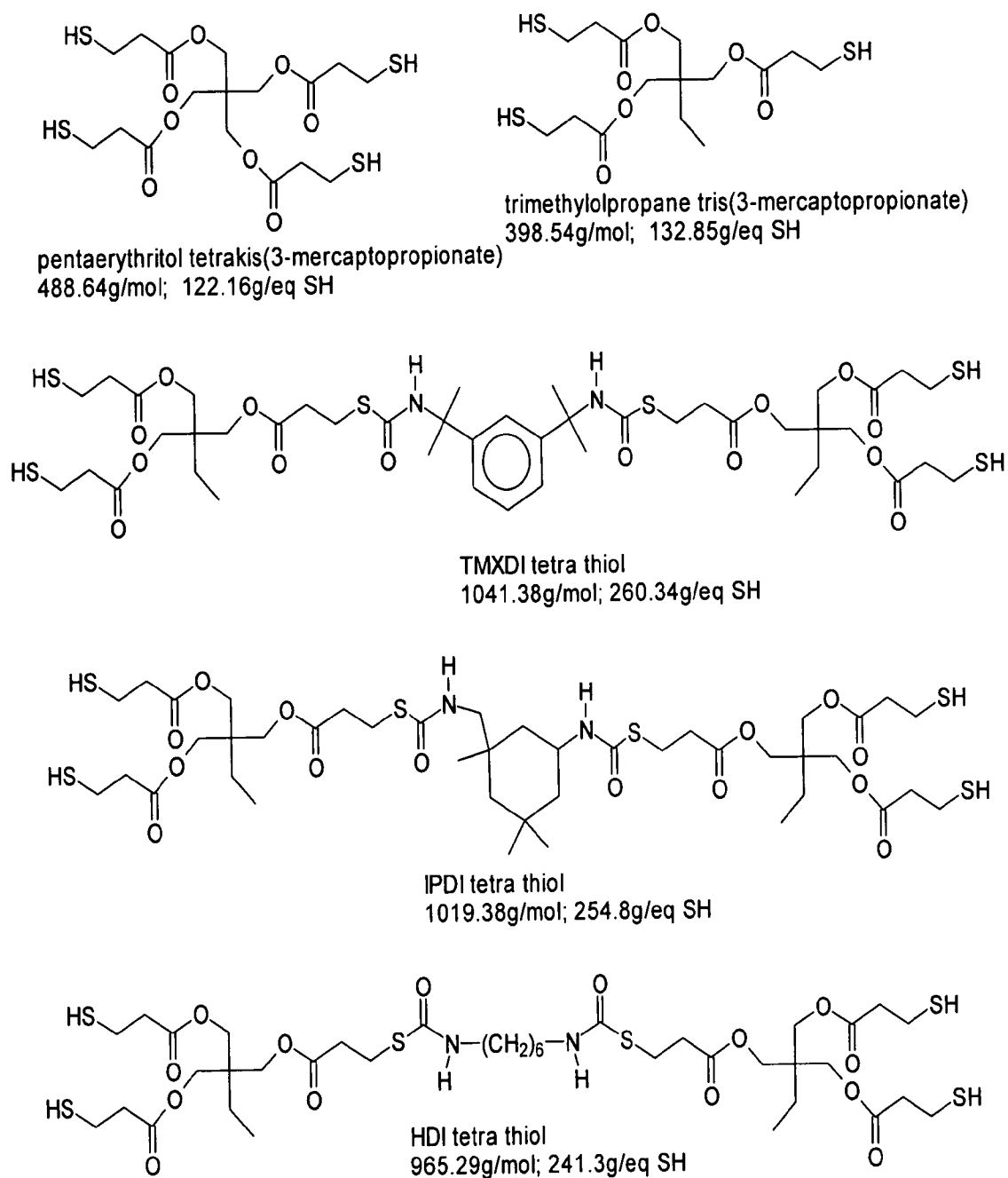


Figure 1. Selected thiols of the invention.

The amounts of the thiol-functional component of the invention preferably ranges from 0.5 to 75wt%, more preferably from 5 to 60 wt%, and most preferably from 20 to 50 wt%., all based on the total weight of the composition.

The ene components of the invention may be any unsaturated compound capable of undergoing free-radical homopolymerization, copolymerization, or polymerization with a thiol through Michael addition and/or free-radical step-growth reactions including vinyl ethers, vinyl esters, allyl esters, allyl ethers, allyl amines, vinyl amines, vinyl amides, esters and amides of (meth)acrylic acid, esters of maleic and fumaric acids, maleimides, et al. One preferred class of enes is (meth)acrylate functional compounds including (meth)acrylated monomers, oligomers, and polymers.

The ene component of the formulations of the invention(s) may be comprised of one or more enes of similar or dissimilar types. Preferred embodiments of the ene components of the present invention(s) include aliphatic urethane (meth)acrylates (ex. EBECRYL[®] 230, EBECRYL[®] 244, EBECRYL[®] 264, EBECRYL[®] 265, EBECRYL[®] 270, EBECRYL[®] 284, EBECRYL[®] 290, EBECRYL[®] 4830, EBECRYL[®] 4833, EBECRYL[®] 8800, EBECRYL[®] 8804, EBECRYL[®] 8807, EBECRYL[®] 8411, EBECRYL[®] 8402, EBECRYL[®] 8405, EBECRYL[®] 8301, available from Cytec Industries, West Paterson, NJ.), and thio-carbamate analogues of those materials. The ene component of the formulation may also contain one or more oligomeric, polymeric, or monomeric enes that do not readily homopolymerize through free-radical chemical processes such as vinyl ethers, N-vinylamides, et al. Norbornenes are also a preferred type of ene in the invention.

Enes may be reacted with other enes and/or with thiols to produce poly-enes of various useful structures. For example, cycloaddition reactions can be utilized to prepare norbornenes through, for example, [4+2] cycloaddition of cyclopentadiene to (meth)acrylates. Similarly, enes with thio-ether functionality may be prepared through Michael addition of poly-thiols with a stoichiometric excess of di or poly-enes such as (meth)acrylates, vinyl acrylate, et al. Selected enes of the invention are listed in Table 2 and Figure 2.

Table 2. Examples of Ene Compounds

NAME	TYPE	Functionality	Mol. Wt.
Trimethylolpropane diallylether	allyl ether	2	214.3
Pentaerythritol triallylether	allyl ether	3	256.34
TMXDI-tetrallylether	allyl ether	4	672.9
IPDI-tetrallylether	allyl ether	4	650.89
H12MDI tetraallylether	allyl ether	4	690.96
HDI hexaallylether	allyl ether	6	680.87
TATATO	allyl ether	3	249.26
Triallyl amine	allyl amine	3	137.22
[3-(Methacryloyloxy)propyl] trimethoxysilane	methacrylate	1	248.35
TMPTA	acrylate	3	296.32
TMPTMA	methacrylate	3	338.4
HDDMA	methacrylate	2	254.32
DiTMPTMA	methacrylate	4	522.63
BADGE dimethacrylate	methacrylate	2	547.1
EBECRYL [®] 3720-TM40	acrylate	2.5	430

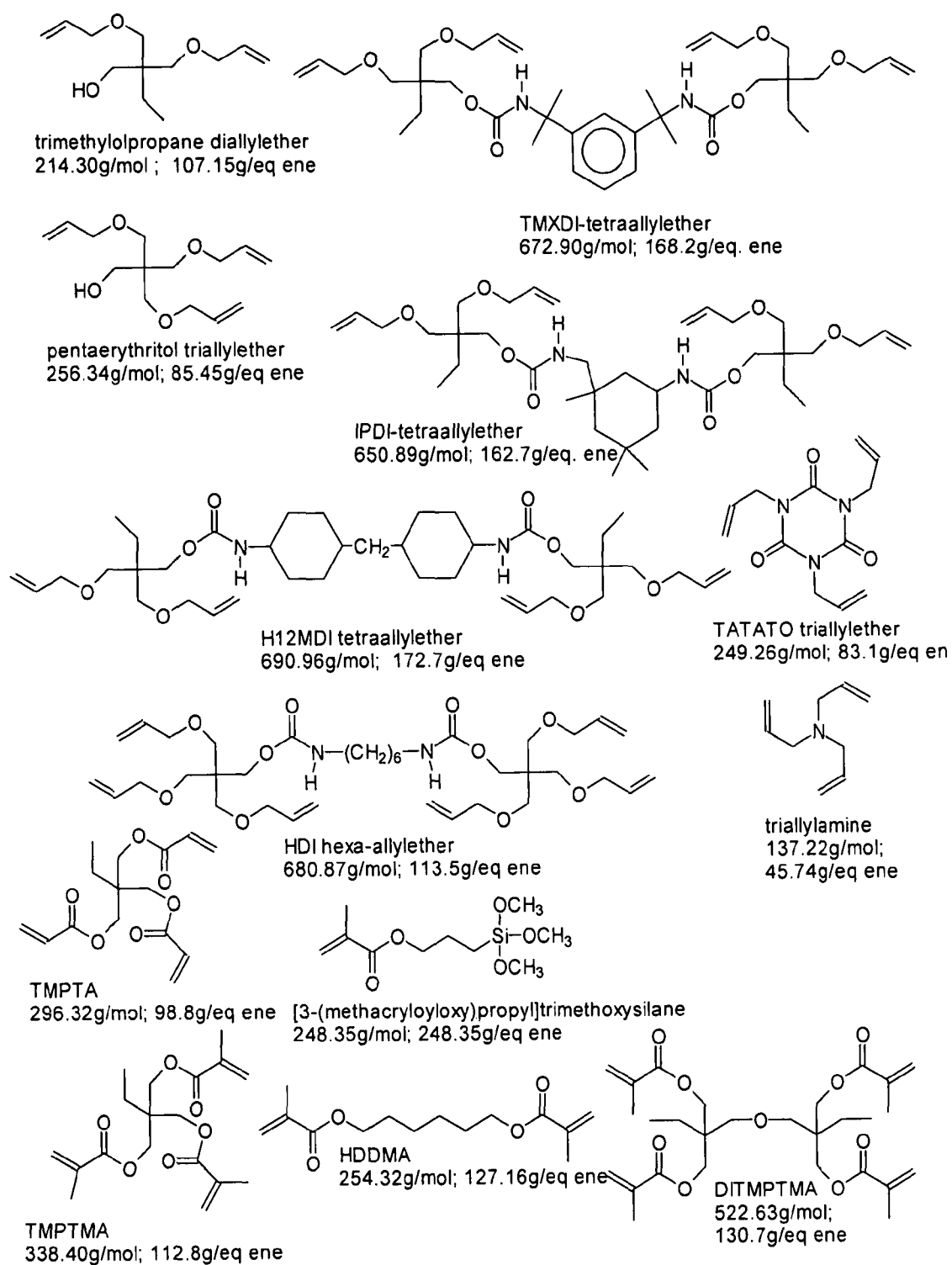


Figure 2. Selected enes of the invention.

In general, the molecular weight of the ene component is preferably 500 g/mol to 20,000 g/mol, and the viscosity is preferably 1000 cP to 10^6 cP (at 25°C). The amounts of the ene component of the invention preferably ranges from 15 to 95 wt%, more preferably from 25 to 75 wt%, and most preferably from 35 to 60 wt%., based on the total weight of the composition.

5 Viscosity being a prime factor in the practical utility of the compositions of the invention, preferred embodiments of the invention also include diluting monomers to control formulation viscosity. These diluting monomers comprise low molecular weight ethylenically unsaturated compounds with molecular weight lower than about 500g/mole and viscosity lower than about 500cP at 25°C, and may include for example: vinyl ethers, vinyl esters, allyl esters, allyl ethers,
10 allyl amines, vinyl amines, vinyl amides, esters and amides of (meth)acrylic acid, esters of maleic and fumaric acids, maleimides, and the like. Preferred diluting monomers include, for example: HDODA, BDODA, PETA, TMPTA, di-TMPTA, TRPGDA, NPGDA, DPGDA, IBOA, ODA-N, EBECRYL® 1040, EBECRYL® 1039, OTA-480, DPHA, acrylate of Cardura E-10P, et al. as well as the corresponding methacrylates. (Meth)acrylic acid is also a preferred
15 diluting monomer of the invention and may functions as an ene and/or as an adhesion promoter.

In general, the molecular weight of the diluting monomeric component is preferably 500 g/mol or less, and the viscosity is preferably 1000 cP or less (at 25°C). The amounts of the diluting monomeric component of the invention ranges from 5 to 90 wt%, more preferably from 20 to 70 wt%, and most preferably from 35 to 55 wt%., based on the total weight of the
20 composition.

It is also anticipated that hybrid and/or dual-cure formulations may be utilized wherein one or more cationically (glycidyl ethers, cycloaliphatic epoxides, etc.), or anionically polymerizable compounds, or compounds that can be polymerized via free-radical and cationic reactions (e.g. vinyl ethers, styryloxy's, propenylethers, et al.) may be advantageously included
25 in the mixture with the thiol or thiol-ene components.

The formulations of the invention optionally may contain a compound that initiates the chemical reactions upon exposure to radiation (visible, UV, infrared, or electron beam), or that initiates the reaction upon exposure to heat. A preferred embodiment of the invention comprises thiol-ene formulations containing free-radical generating cleavage and hydrogen-abstraction type
30 photoinitiators such as Additol TPO (Cytec Industries Inc.); Additol BCPK (Cytec Industries Inc.); Additol BDK (Cytec Industries Inc.); Additol HDMAP (Cytec Industries Inc.); Additol

ITX (Cytec Industries Inc.); Additol CPK (Cytec Industries Inc.); Additol BP (Cytec Industries Inc.); and the like. In formulations of the inventions containing cationically polymerizable ene or epoxy components, a photo-acid generating initiator may optionally included, selected from, for example, sulphonium salts, iodoium salts, and other compounds known or reasonably
5 expected to initiate a cationic polymerization. Optionally, one or more photo-base generators which produce Lewis base upon irradiation may be used, particularly in anionically polymerizable hybrid formulations of the invention.

The formulations of the inventions may also contain stabilizers to prevent premature reaction of the formulation. These stabilizers may be antioxidants, free-radical scavengers, UV-
10 absorbers, and/or other known stabilizers including for example compounds selected from: hydroquinone type compounds, phenolics, nitrosoamines, thiazines, thioesters, phosphites, antimony compounds, hindered amine light stabilizers (HALS), and the like, including for example: hydroquinone (HQ); 4-methoxyphenol (MEHQ); 2,6-di-t-butyl-4-methylphenol (BHT); 2-methyl-1,4-benzenediol (THQ); phenothiazine (PTZ), tris(N-nitroso-N-
15 phenylhydroxyamine) aluminum salt (NPAL, Albemarle Corp.); CYANOX[®] 425 (Cytec Industries Inc.); CYANOX[®] 1741(Cytec Industries Inc.); CYANOX[®] 1790(Cytec Industries Inc.); CYANOX[®] 2246(Cytec Industries Inc.); CYANOX[®] 711(Cytec Industries Inc.); CYANOX[®] 1212 (Cytec Industries Inc.); CYANOX[®] LTDP(Cytec Industries Inc.); CYANOX[®] STDP(Cytec Industries Inc.); CYANOX[®] 2777(Cytec Industries Inc.); CYANOX[®] XS4(Cytec
20 Industries Inc.); CYASORB[®] UV-2337(Cytec Industries Inc.); CYASORB[®] UV-5411(Cytec Industries Inc.); CYASORB[®] UV-594; CYASORB[®] UV-9(Cytec Industries Inc.); CYASORB[®] UV-24(Cytec Industries Inc.); CYASORB[®] UV-531(Cytec Industries Inc.); CYASORB[®] UV-2126(Cytec Industries Inc.).

Optionally, for formulations of the invention that contain cationically polymerizable
25 components, an acid-scavenging stabilizer may be included to prevent premature cationic polymerization or oligomerization of the formulation. While use of a shelf-stable fully formulated thiol-ene component resin mixture is preferred, a possible embodiment may include a multi-component system that must be mixed by the end-user just prior to use.

The composition of the invention(s) optionally may contain additives to increase
30 adhesion of the cured interlayer to the glass or polymer lites. These additives may be selected from a range of compound types may include for example, free-radically or cationically

polymerizable compounds with secondary functionality selected from one or more of the following types: silane, siloxane, phosphonate, phosphate, sulfonate, amine, thio-ether, urethane, urea, thiocarbamate, thiourea, carboxylic acid. Other additives, such as colorants, flow-aides, dispersing aides, foam-control agents, surfactants, antioxidants, light stabilizers, and others
5 known in the field including inert fillers such as silica, alumina, titanium dioxide, pigments, dyes, clays, acrylic polymers, and similar materials may optionally be included in the compositions of the invention.

The amounts of these additional ingredients preferably ranges from 0.005 to 25 wt%, more preferably from 0.01 to 10 wt%, and most preferably from 0.025 to 5 wt%.

10 The compositions of the present invention are prepared using methods known in the art. For example, in the Examples described below, glass laminates are made by sandwiching two panes (lites) of heat treated or annealed glass wherein the lites are separated around the perimeter by a spacer tape with thickness of 0.76 mm to 3mm, and then filling the interstitial volume with the compositions of the invention by pumping the resin into the cavity with the sandwiched lites
15 standing at an angle of at least 60°. After filling with the proper volume of liquid, the filled sandwich is slowly returned to horizontal, allowing the liquid to flow throughout the entire cavity. When the liquid reaches the filling opening, the opening is sealed with hot melt material. Any entrapped air is then removed with a small syringe. The polymer interlayer is then formed through exposure of the sandwiched resin composition to irradiation under a bank of fluorescent
20 UV-A bulbs for 20 minutes.

Polymerization, or cure, of the formulations of the invention may be accomplished by exposure of the resin mixture to electromagnetic radiation in the ultraviolet, visible, or infrared spectral regions. Polymerization may also be conducted thermally alone, or in combination with electromagnetic irradiation. Optionally the formulations of the invention may be cured via
25 electron-beam irradiation. While the most preferred method of cure is irradiation by UV-A fluorescent bulbs, preferred methods also include exposure to solar radiation (e.g. sunshine), LED lamps, or emissions from doped or undoped mercury arc lamps (medium pressure, high pressure), microwave lamps (Fusion D, H, V, excimer bulbs), and other gas plasma sources.

The laminates of the invention are preferably constructed to be translucent to the curing
30 radiation from either face of the laminate. Optionally, the laminates may be opaque on both

faces, in which case the cure may be accomplished thermally, by electron beam, or by exposure of the laminate edge to irradiation.

Products that may be made from the composition of the invention include laminate structures wherein two or more glass and/or polymeric substrates are adhered together in a layered arrangement such that the polymerized compositions of this invention form one or more polymeric interlayer(s) interspaced between adjacent glass or polymeric substrates. For example, two glass panes could form a sandwich of the composition of the invention.

Alternatively, two polymeric panes could be used to form such a sandwich, or a combination of glass and polymeric panes. Construction of the products of the invention may be conducted via standard UVEKOL[®] S type manufacturing processes or other processes known in the art. In a given product, the substrate layers may be colored or colorless, translucent, opaque, reflective, painted, decorated, or printed. Optionally the polymeric interlayer(s) may be colored or colorless, translucent or opaque.

The present invention also includes machines or articles of manufacture incorporating the above laminates. The composition of the invention is particularly useful in the production of glass laminates for hurricane glass, bullet resistant glazing and/or polymer laminates for window or structural applications, acoustical dampening laminates for window applications, and safety glass for automotive or architectural applications. Particular applications of the composition of the invention is in producing windows designed for protection against ballistic impact of bullets or other projectiles, and windows designed for protection against overpressures generated by detonation of bombs and other explosive devices.

EXAMPLES

The following examples are intended to illustrate, but in no way limit the scope of the present invention. All parts and percentages are by weight, and temperatures are in degrees Celsius unless explicitly stated otherwise.

COMPOSITION 1

Composition 1 includes tetrathiol/triallylether components in a 1:1 equivalent ratio plus 30% by wt. di/tri methacrylate as follows:

Raw material	Primary function	Functional Groups	Wt %
pentaerythritol tetrakis(3-mercaptopropionate)	thiol	4	36.1
trimethylolpropane diallylether	Allyl ether	2	31.6
TMPTMA	methacrylate	3	10
HDDMA	methacrylate	2	20
[3-(methacryloyloxy)propyl] trimethoxysilane	methacrylate	1	1
NPAL	stabilizer		1
Additol CPK			0.3

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Composition 1 is prepared by admixture of 31.6g trimethylolpropane diallylether with 10g trimethylolpropane trimethacrylate, 20g 1,6-hexanedioldimethacrylate, 1g [3-(methacryloyloxy)propyl] trimethoxysilane, and 36.1g of pentaerythritol tetrakis(3-mercaptopropionate) under low-shear mixing conditions at for 1 hour at 25°C. To this homogeneous mixture is added 1g NPAL (Albemarle Corp.) and 0.3g Additol CPK (Cytec Industries, Inc.) followed by further mixing at 25°C until homogeneous.

10

COMPOSITION 2

Composition 2 includes tetrathiol/tetra allylether urethane in a 1:1 equivalent ratio plus 20% by wt. dimethacrylate as follows:

15

Raw material	Primary function	Functional Groups	Wt %
pentaerythritol tetrakis(3-mercaptopropionate)	thiol	4	32.7
TMXDI-tetraallylether	Allyl ether	4	45
HDDMA	methacrylate	2	20
[3-(methacryloyloxy)propyl] trimethoxysilane	methacrylate	1	1
NPAL	stabilizer		1
Additol CPK			0.3

Composition 2 is prepared as follows. 16.34g TMXDI diisocyanate (CYTEC) and 20g 1,6-hexanedioldimethacrylate are added to a reaction flask and mixed at 25°C. 0.1g dibutyltindilaurate and 0.2g methoxyphenol are added to the mixture and mixed until
 5 homogenous. 28.66g trimethylolpropane diallylether is then added dropwise to the stirring reaction mixture over 1 hour, after which the reaction mixture is heated to 60°C and held until all of the isocyanate has been consumed. The reaction mixture is cooled to 25°C, and is designated TMXDI-tetrallylether. 1g NPAL (Albemarle Corp.), 0.3g Additol CPK (Cytec Industries, Inc.), and 32.7g pentaerythritol tetrakis(3-mercaptopripionate), and 1g [3-(methacryloyloxy)propyl]
 10 trimethoxysilane are added to the reaction flask and mixed until homogeneous.

COMPOSITION 3

Composition 3 includes tetrathiol/tetraallyl ether urethane in a 1:1 equivalent ratio plus 20% by wt dimethacrylate as follows:

Raw material	Primary function	Functional groups	Wt %
pentaerythritol tetrakis(3-mercaptopripionate)	Thiol	4	32.2
H12MDI tetraallylether	allyl ether	4	45.5
HDDMA	methacrylate	2	20
[3-(methacryloyloxy)propyl] trimethoxysilane	methacrylate	1	1
NPAL	stabilizer		1
Additol CPK			0.3

Composition 3 is prepared as follows. 17.29g Desmodur W diisocyanate (Bayer) and 20g 1,6-hexanedioldimethacrylate are added to a reaction flask and mixed at 25°C. 0.1g dibutyltindilaurate and 0.2g 4-methoxyphenol are added to the mixture and mixed until
 20 homogenous. 28.21g trimethylolpropane diallylether is then added dropwise to the stirring reaction mixture over 1 hour, after which the reaction mixture is heated to 60°C and held until all of the isocyanate has been consumed. The reaction mixture is cooled to 25°C, and is designated H12MDI-tetrallylether. 1g NPAL (Albemarle Corp.), 0.3g Additol CPK (Cytec Industries Inc.),

and 32.2g pentaerythritol tetrakis(3-mercaptopropionate), and 1g [3-(methacryloyloxy)propyl] trimethoxysilane are added to the reaction flask and mixed until homogeneous.

COMPOSITION 4

- 5 Composition 4 includes trithiol/tetraallylether urethane in a 1:1 equivalent ratio plus 30% by wt. di/tetra methacrylate as follows:

Raw material	Primary function	Functional groups	Wt %
trimethylopropane tris(3-mercaptopropionate)	Thiol	3	29.4
H12MDI tetraallylether	allyl ether	4	38.3
HDDMA	methacrylate	2	20
DiTMPTMA	methacrylate	4	10
[3-(methacryloyloxy)propyl] trimethoxysilane	methacrylate	1	1
NPAL	stabilizer		1
Additol CPK			0.3

- Composition 4 is prepared as follows. 14.55g Desmodur W diisocyanate (Bayer) and
 10 20g 1,6-hexanedioldimethacrylate are added to a reaction flask and mixed at 25°C. 0.1g dibutyltindilaurate and 0.2g 4-methoxyphenol are added to the mixture and mixed until homogenous. 23.75g trimethylolpropane diallylether is then added dropwise to the stirring reaction mixture over 1 hour, after which the reaction mixture is heated to 60°C and held until all of the isocyanate has been consumed. The reaction mixture is cooled to 25°C, and is designated
 15 H12MDI-tetraallylether. 1g NPAL (Albemarle Corp.), 0.3g Additol CPK (Cytec Industries Inc.), 10g di-trimethylolpropane tetramethacrylate, and 29.4g trimethylopropane tris(3-mercaptopropionate), and 1g [3-(methacryloyloxy)propyl] trimethoxysilane are added to the reaction flask and mixed until homogeneous.

COMPOSITION 5

Composition 5 includes tetrathiol/tetraallylether urethane in a 1:1 equivalent ratio plus 20% dimethacrylate plus 20% UA oligomer as follows:

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Raw material	Primary function	Functional groups	Wt %
pentaerythritol tetrakis(3-mercaptopropionate)	thiol	4	23.9
H12MDI tetraallylether	allyl ether	4	33.8
HDDMA	methacrylate	2	20
EBECRYL [®] 230	acrylate	2	20
[3-(methacryloyloxy)propyl] trimethoxysilane	methacrylate	1	1
NPAL	stabilizer		1
Additol CPK			0.3

Composition 5 is prepared as follows. 12.84g Desmodur W diisocyanate (Bayer) and 20g 1,6-hexanedioldimethacrylate are added to a reaction flask and mixed at 25°C. 0.1g dibutyltindilaurate and 0.2g 4-methoxyphenol are added to the mixture and mixed until

10 homogenous. 20.96g trimethylolpropane diallylether is then added dropwise to the stirring reaction mixture over 1 hour, after which the reaction mixture is heated to 60°C and held until all of the isocyanate has been consumed. The reaction mixture is cooled to 25°C, and is designated H12MDI-tetraallylether. 1g NPAL (Albemarle Corp.), 0.3g Additol CPK (Cytec Industries Inc.), 20g EBECRYL[®] 230 (CYTEC), and 23.9g pentaerythritol tetrakis(3-mercaptopropionate), and

15 1g [3-(methacryloyloxy)propyl] trimethoxysilane are added to the reaction flask and mixed until homogeneous.

COMPOSITION 6

Composition 6 includes tetrathiol urethane/triazine triallylether (1:1 equivalents) plus 30% HDDDA, 20% EB230 as follows:

5

Raw material	Primary function	Functional groups	Wt %
IPDI tetra thiol	thiol	4	36
TATATO	allyl ether	3	11.7
HDDA	acrylate	2	30
EBECRYL [®] 230	acrylate	2	20
[3-(methacryloyloxy)propyl] trimethoxysilane	methacrylate	1	1
NPAL	stabilizer		1
Additol CPK			0.3

Composition 6 is prepared as follows. 28.14g trimethylopropane tris(3-mercaptopropionate) is added to a reaction flask. 0.05g dibutyltindilaurate and 0.2g 4-methoxyphenol are added and mixed at 25°C until homogenous. 7.86g isophorone diisocyanate (Bayer) is then added dropwise to the stirring reaction mixture over 1 hour, after which the reaction mixture is heated to 60°C and held until all of the isocyanate has been consumed. The reaction mixture is cooled to 25°C, and is designated IPDI tetra thiol. 1g NPAL (Albemarle Corp.), 0.3g Additol CPK (Cytec Industries Inc.), 20g EBECRYL[®] 230 (CYTEC), 30g 1,6-hexanedioldiacrylate, 11.7g 1,3,5-triallyl-1,3,5-triazine-2,4,6-(1H, 3H, 5H)-trione, and 1g [3-(methacryloyloxy)propyl] trimethoxysilane are added to the reaction flask and mixed until homogeneous.

COMPOSITION 7

Composition 7 includes tetrathiol urethane/triazine triallylether (1:1 equivalents) plus 30% HDDMA, 15% EBECRYL[®] 230, 10% EBECRYL[®] 3720-TM40 as follows:

5

Raw material	Primary function	Functional groups	Wt %
IPDI tetra thiol	thiol	4	32.2
TATATO	allyl ether	3	10.5
HDDMA	methacrylate	2	30
EBECRYL 3720-TM40	acrylate	2.5	10
EBECRYL [®] 230	acrylate	2	15
[3-(methacryloyloxy)propyl] trimethoxysilane	methacrylate	1	1
NPAL	stabilizer		1
Additol CPK			0.3

Composition 7 is prepared as follows. 25.17g trimethylopropane tris(3-mercaptopropionate) is added to a reaction flask. 0.05g dibutyltin dilaurate and 0.2g 4-methoxyphenol are added and mixed at 25°C until homogenous. 7.03g isophorone diisocyanate (Bayer) is then added dropwise to the stirring reaction mixture over 1 hour, after which the reaction mixture is heated to 60°C and held until all of the isocyanate has been consumed. The reaction mixture is cooled to 25°C, and is designated IPDI tetra thiol. 1g NPAL (Albemarle Corp.), 0.3g Additol CPK (Cytec Industries Inc.), 15g EBECRYL[®] 230 (CYTEC), 30g 1,6-hexanedioldimethacrylate, 10g EBECRYL[®] 3720-TM40 (CYTEC), 10.5g 1,3,5-triallyl-1,3,5-triazine-2,4,6-(1H, 3H, 5H)-trione, and 1g [3-(methacryloyloxy)propyl] trimethoxysilane are added to the reaction flask and mixed until homogeneous.

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COMPOSITION 8

Composition 8 includes tetrathiol/tetraallylether urethane (1:1 equivalents) plus 25% TCDDMDMA, 20% EBECRYL[®] 230, and 10% methylmethacrylate.

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Raw material	Primary function	Functional groups	Wt %
pentaerythritol tetrakis(3-mercaptopropionate)	thiol	4	18
TMXDI-tetraallylether	allyl ether	4	24.7
tricyclodecanedimethanol dimethacrylate	methacrylate	2	25
Methylmethacrylate	methacrylate	1	10
EBECRYL [®] 230	acrylate	2	20
[3-(methacryloyloxy)propyl] trimethoxysilane	methacrylate	1	1
NPAL	stabilizer		1
Additol CPK			0.3

Composition 8 is prepared as follows. 8.97g TMXDI diisocyanate (Cytec Industries, Inc.) and 10g methylmethacrylate are added to a reaction flask and mixed at 25°C. 0.02g dibutyltin dilaurate and 0.1g 4-methoxyphenol are added to the mixture and mixed until homogenous. 15.73g trimethylolpropane diallylether is then added dropwise to the stirring reaction mixture over 1 hour, after which the reaction mixture is heated to 60°C and held until all of the isocyanate has been consumed. The reaction mixture is cooled to 25°C, and is designated TMXDI-tetraallylether. 1g NPAL (Albemarle Corp.), 0.3g Additol CPK (Cytec Industries Inc.), and 18g pentaerythritol tetrakis(3-mercaptopropionate), 25g tricyclodecane-dimethanoldimethacrylate, 20g EBECRYL[®] 230 (Cytec) and 1g [3-(methacryloyloxy)propyl] trimethoxysilane are added to the reaction flask and mixed until homogeneous.

COMPOSITION 9

Composition 9 includes tetrathiol/hexylallylether urethane (1:1 equivalents) plus 20% TMPTMA, 20% EHA, 5% MAA, and 10% EBECRYL[®] 230.

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Raw material	Primary function	Functional groups	Wt %
pentaerythritol tetrakis(3-mercaptopropionate)	thiol	4	22.1
HDI hexaallylether	allyl ether	6	20.6
TMPTMA	methacrylate	3	20
Ethylhexylacrylate	acrylate	1	20
methacrylic acid	methacrylate	1	5
EBECRYL [®] 230	acrylate	2	10
[3-(methacryloyloxy)propyl] trimethoxysilane	methacrylate	1	1
NPAL	stabilizer		1
Additol CPK			0.3

Composition 9 is prepared as follows. 5.09g hexamethylene diisocyanate (Bayer) and 20g ethylhexylacrylate are added to a reaction flask and mixed at 25°C. 0.02g dibutyltindilaurate and 0.1g 4-methoxyphenol are added to the mixture and mixed until homogenous. 15.51g pentaerythritol tetraallylether is then added dropwise to the stirring reaction mixture over 1 hour, after which the reaction mixture is heated to 60°C and held until all of the isocyanate has been consumed. The reaction mixture is cooled to 25°C, and is designated HDI hexa-allylether. 1g NPAL (Albemarle Corp.), 0.3g Additol CPK (Cytec Industries Inc.), 22.1g pentaerythritol tetrakis(3-mercaptopropionate), 20g trimethylolpropanetrimethacrylate, 10g EBECRYL[®] 230 (Cytec), 5g methacrylic acid, and 1g [3-(methacryloyloxy)propyl] trimethoxysilane are added to the reaction flask and mixed until homogeneous.

COMPOSITION 10

Composition 10 includes tetrathiol/tetraallylether urethane (1:1 equivalents) plus 20% TMPTMA, 15% MMA, and 20% EBECRYL[®] 8302.

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Raw material	Primary function	Functional groups	Wt %
pentaerythritol tetrakis(3-mercaptopropionate)	thiol	4	25
H12MDI tetraallylether	allyl ether	4	17.7
TMPTMA	methacrylate	3	20
methylmethacrylate	methacrylate	1	15
EBECRYL [®] 8302	acrylate	3.5	20
[3-(methacryloyloxy)propyl]trimethoxysilane	methacrylate	1	1
NPAL	stabilizer		1
Additol CPK			0.3

Composition 10 is prepared as follows. 6.72g Desmodur W diisocyanate (Bayer) and 15g methylmethacrylate are added to a reaction flask and mixed at 25°C. 0.05g dibutyltindilaurate and 0.2g 4-methoxyphenol are added to the mixture and mixed until
10 homogenous. 10.98g trimethylolpropane diallylether is then added dropwise to the stirring reaction mixture over 1 hour, after which the reaction mixture is heated to 60°C and held until all of the isocyanate has been consumed. The reaction mixture is cooled to 25°C, and is designated H12MDI-tetraallylether. 1g NPAL (Albemarle Corp.), 0.3g Additol CPK (Cytec Industries Inc.), 20g EBECRYL[®] 8302 (CYTEC), 20g trimethylolpropane trimethacrylate, 25g pentaerythritol
15 tetrakis(3-mercaptopropionate), and 1g [3-(methacryloyloxy)propyl] trimethoxysilane are added to the reaction flask and mixed until homogeneous.

COMPOSITION 11

Composition 11 includes tetrathiol urethane/triallylamine (1:1 equivalents) plus 20% DiTMPTMA, 15% MMA, and 20% EBECRYL[®] 8405.

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Raw material	Primary function	Functional groups	Wt %
IPDI tetra thiol	thiol	4	38.1
triallyl amine	allyl amine	3	4.6
DiTMPTMA	methacrylate	4	20
methylmethacrylate	methacrylate	1	15
EBECRYL [®] 8405	acrylate	4	20
[3-(methacryloyloxy)propyl] trimethoxysilane	methacrylate	1	1
NPAL	stabilizer		1.5
Additol CPK			0.3

Composition 11 is prepared as follows. 29.78g trimethylopropane tris(3-mercaptopropionate) is added to a reaction flask. 0.05g dibutyltindilaurate and 0.2g 4-methoxyphenol are added and mixed at 25°C until homogenous. 8.32g isophorone diisocyanate (Bayer) is then added dropwise to the stirring reaction mixture over 1 hour, after which the reaction mixture is heated to 60°C and held until all of the isocyanate has been consumed. The reaction mixture is cooled to 25°C, and is designated IPDI tetra thiol. 1.5g NPAL (Albemarle Corp.), 0.3g Additol CPK (Cytec Industries Inc.), 4.6g triallylamine, 20g di-trimethylolpropane tetramethacrylate, 20g EBECRYL[®] 8405 (CYTEC), 15g methylmethacrylate, and 1g [3-(methacryloyloxy)propyl] trimethoxysilane are added to the reaction flask and mixed until homogeneous.

While the invention has been described above with reference to specific embodiments thereof, it is apparent that many changes, modifications, and variations can be made without departing from the inventive concept disclosed herein. Accordingly, it is intended to embrace all such changes, modifications, and variations that fall within the spirit and broad scope of the appended claims. All patent applications, patents, and other publications cited herein are incorporated by reference in their entireties.

CLAIMS

WHAT IS CLAIMED IS:

- 5 1. A laminate composition, comprising:
- (1) one or more thiol-functional compounds;
 - (2) one or more oligomeric or polymeric compounds containing one or more carbon-carbon double bonds or triple bonds; and
 - (3) one or more monomeric compounds containing one or more carbon-carbon
- 10 double bonds or triple bonds.
2. The laminate composition of claim 1, wherein said thiol-functional compound is poly thiol-functional.
- 15 3. The laminate composition of claim 2, wherein said poly thiol functional compound contains 3 or more thiol groups per molecule.
4. The laminate composition of claim 1, wherein said thiol-functional compound is selected from the group consisting of pentaerythritol tetrakis [3-mercaptopropionate], trimethylolpropane
- 20 tris[3-mercaptopropionate], TMXDI tetra thiol, IPDI tetra thiol, HDI tetra thiol, hexanedithiol, ethyleneglycol di-2-mercaptoacetate, pentaerythritol tetrakis(2-mercaptoacetate), trimethylolpropane tris(2-mercaptoacetate), ethyleneglycol di-3-mercaptopropionate, and combinations thereof.
- 25 5. The laminate composition of claim 1, wherein said thiol-functional component comprises from 0.5 to 75wt%, more preferably from 5 to 60 wt%, and most preferably from 20 to 50 wt%., all based on the total weight of said laminate composition.
6. The laminate composition of claim 1, wherein said oligomeric or polymeric compounds
- 30 containing one or more carbon-carbon double bonds or triple bonds is selected from the group consisting of allyl ethers, acrylates, and methacrylates.

7. The laminate composition of claim 1, wherein said oligomeric or polymeric compounds containing one or more carbon-carbon double bonds or triple bonds is selected from the group consisting of trimethylolpropane diallylether, pentaerythritol triallylether, TMXDI-tetrallylether, 5 IPDI-tetrallylether, H12MDI tetraallylether, HDI hexaallylether, TATATO, triallyl amine, [3-(methacryloyloxy)propyl]trimethoxysilane, TMPTA, TMPTMA, HDDMA, DiTMPTMA, BADGE dimethacrylate, EBECRYL[®] 3720-TM40, and combinations thereof.

8. The laminate composition of claim 1, wherein said oligomeric or polymeric compounds 10 containing one or more carbon-carbon double bonds or triple bonds comprise from 15 to 95 wt%, more preferably from 25 to 75 wt%, and most preferably from 35 to 60 wt%., based on the total weight of the composition.

9. The laminate composition of claim 1, wherein said one or more monomeric compounds 15 containing one or more carbon-carbon double bonds or triple bonds is selected from the group consisting of vinyl ethers, vinyl esters, allyl esters, allyl ethers, allyl amines, vinyl amines, vinyl amides, esters and amides of (meth)acrylic acid, esters of maleic and fumaric acids, maleimides, HDODA, BDODA, PETA, TMPTA, di-TMPTA, TRPGDA, NPGDA, DPGDA, IBOA, ODA-N, EBECRYL[®] 1040, EBECRYL[®] 1039, OTA-480, DPHA, acrylate of Cardura E-10P, and their 20 corresponding methacrylates.

10. The laminate composition of claim 1, wherein said one or more monomeric compounds containing one or more carbon-carbon double bonds or triple bonds comprise from 5 to 90 wt%, more preferably from 20 to 70 wt%, and most preferably from 35 to 55 wt%., based on the total 25 weight of the composition.

11. The laminate composition of claim 1, further comprising optional additional ingredients selected from the group consisting of one or more monomeric or oligomeric compounds containing epoxy or glycidylether groups, photoinitiators, thermal initiators, photoacid 30 generators, photobase generators, stabilizers, pigments, dyes, coloring agents, surfactants, and combinations thereof.

12. A method of producing a laminate, comprising the steps of:

(1) providing at least two juxtaposed panes of glass and/or polymer having a gap between them;

5 (2) applying a laminate composition according to any of claims 1 to 11 into said gap; and
(3) curing said composition.

13. The method of claim 12, wherein said curing step comprises ultraviolet, visible, infrared, electromagnetic irradiation, electron beam, or heating.

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14. A laminate, comprising at least two juxtaposed panes of glass and/or polymer having a gap between them, said gap filled with the composition of claim 1 in a cured state.

15. A machine or article of manufacture incorporating the laminate of claim 14, and
15 comprising a window, door, or curtainwall designed for use in hurricane conditions, for acoustical dampening, for protection against ballistic impact of bullets or other projectiles, for protection against overpressures generated by detonation of bombs and other explosive devices, for use in safety and security applications, and/or for use in fire resistant applications.

INTERNATIONAL SEARCH REPORT

CORRECTED VERSION

International application No

PCT/EP2008/058856

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09D181/04 B32B17/10 C03C27/12
 ADD. C08G75/04

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G C09D B32B

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

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

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 190 992 A (KATO TOSHIYUKI [US] ET AL) 2 March 1993 (1993-03-02) column 3, line 5 - column 4, line 58; examples 5,6	1,2,5,6, 8,10,11
X	column 5, line 25 - line 56 -----	12-15
X	US 4 272 586 A (ANDO TOSHIHIRO ET AL) 9 June 1981 (1981-06-09) column 8, line 1 - column 9, line 62; examples 4-6; table 5 claims	1-14
A	----- US 5 411 776 A (SCHMIDT GERALD [DE] ET AL) 2 May 1995 (1995-05-02) claims; examples ----- -/--	1-15

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

9 October 2008

Date of mailing of the international search report

19.12.08

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040,
 Fax: (+31-70) 340-3016

Authorized officer

Lindner, Thomas

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2008/058856

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 5 876 805 A (OSTLIE BRIAN W [US]) 2 March 1999 (1999-03-02) column 1, line 9 - column 4, line 24 column 6; table 1 column 8, line 1 - line 37 column 11; example 1; table I claims; examples 4,7; table VI -----	1-11
X	US 4 587 313 A (OHTA TOMOHISA [JP] ET AL) 6 May 1986 (1986-05-06) claims; examples 1,2 -----	1-6,8-11
X	US 6 669 873 B1 (SMITH ROBERT A [US] ET AL) 30 December 2003 (2003-12-30) column 1, line 10 - column 3, line 18 column 17, line 13 - column 20, line 5 -----	1,2,4,6, 8,10,11
A	US 6 479 622 B1 (GROSS KATHLEEN B [US] ET AL) 12 November 2002 (2002-11-12) column 7, line 15 - column 9, line 5; example 5 -----	1-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2008/058856

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5190992	A	02-03-1993	NONE	
US 4272586	A	09-06-1981	DE 2907176 A1	30-08-1979
US 5411776	A	02-05-1995	DE 4311185 A1	13-10-1994
			EP 0619355 A1	12-10-1994
			JP 2804955 B2	30-09-1998
			JP 7097561 A	11-04-1995
US 5876805	A	02-03-1999	BR 9708589 A	03-08-1999
			CA 2248616 A1	16-10-1997
			CN 1215421 A	28-04-1999
			EP 0883653 A1	16-12-1998
			JP 2000508685 T	11-07-2000
			KR 20000005235 A	25-01-2000
			WO 9738054 A1	16-10-1997
US 4587313	A	06-05-1986	NONE	
US 6669873	B1	30-12-2003	AU 762655 B2	03-07-2003
			AU 4472300 A	10-11-2000
			BR 0011151 A	19-04-2005
			DE 60020963 D1	28-07-2005
			DE 60020963 T2	18-05-2006
			EP 1177241 A1	06-02-2002
			ES 2243258 T3	01-12-2005
			JP 2004511578 T	15-04-2004
			WO 0064964 A1	02-11-2000
US 6479622	B1	12-11-2002	US 2003144442 A1	31-07-2003
			US 2003144443 A1	31-07-2003
			US 2003144444 A1	31-07-2003
			US 2003144445 A1	31-07-2003
			US 6605692 B1	12-08-2003