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(54) **Title**: SULFUR MODIFIED SILANES FOR THE ELABORATION OF HIGH REFRACTIVE INDEX MATERIALS

(57) **Abstract**: A composition having a polysulfide polysilane formed by the reaction of a polythiol and an alkenyl silane. The reactants are combined in a thiol-ene addition process driven by UV radiation or heat, preferably by UV radiation. The polysulfide polysilane is then hydrolyzed and may be combined with other hydrolyzed compounds. For coatings, the polysulfide polysilane is hydrolyzed and may optionally be combined with nanoparticles. For bulk materials, the polysulfide polysilane is hydrolyzed, concentrated and heated to form a high refractive index material which can be used to form lenses.

SULFUR MODIFIED SILANES FOR THE ELABORATION OF HIGH REFRACTIVE INDEX MATERIALS

The present invention relates generally to high refractive index materials, and processes for synthesizing them, and applications for using them as optical bulk materials or high index coatings which are preferably hard coatings.

For ophthalmic lenses, plastic materials represent a safer, thinner and lightweight alternative. Such plastic ophthalmic lenses frequently have a surface coating to provide scratch resistance or to impart functional optical features such as tints or anti-reflective surfaces.

Silane based matrices can be used for both coatings and bulk materials. These silanes have reasonably good mechanical properties, but suffer from relatively low refractive index (RI) values, between 1.42 and 1.55. As the demand for thinner and lighter lenses increases, there is a greater need for materials having a higher index of refraction and better mechanical properties. The eye lens industry is focusing on producing high index lenses (refractive index, about 1.6-1.7), which require correspondingly high refractive index (1.63-1.68) coatings. The refractive index of presently available organic coatings is about 1.5, making them unsuitable for high index lenses. Therefore, there is an immediate need for optical grade coatings that have high refractive index.

Plastic lens usually have refractive index as high as 1.67, 1.74 or even 1.80. Conventional coatings usually have a low refractive index of about 1.50. The large difference between the lens substrate refractive index and the coating refractive index causes unsightly fringes. Therefore, it would be desirable to have higher index coatings, and hybrid coatings with correspondingly improved mechanical properties.

One prior hybrid coating is disclosed in US Published Application 2005/0123771. An epoxy silane is hydrolyzed and combined with colloidal silica and an aluminum compound, like an aluminum chelate. The composition has application as an abrasion resistant coating and is useful when applied in conjunction with nonreflective coating layers. Another prior art example s described in US Published Application 2003/165698.

An example of prior art bulk materials is the class of organic polymers. Organic polymers based on thiols and thio-ethers provide a high refractive index (up to 1.70) but are purely organic and not hybrid organic-inorganic. Mechanical properties can be improved by introducing inorganic nanoparticles, however the resulting material is usually hazy due to nanoparticles aggregation.

Hybrid materials, such as transparent hybrid bulk materials are known to be made from silanes leading to an inorganic network. In that case the refractive index is low. The refractive index can be increased slightly by introducing metal alkoxides. However in this case huge differences in kinetics lead to precipitation of the metal alkoxide, limiting the per cent of metal alkoxide content or leading to hazy materials. A prior bulk material is disclosed in US Patent 6,624,237 by hydrolyzing an organo-silicon monomer. The monomer may be combined with an epoxy silane or photochromic compound before hydrolyzing. Another prior art example is described in WO94/25406, which discusses the sol-gel process.

An example of prior art silane coatings is glycidoxypropyltrimethoxysilane, which is referred to by the commercial name Glymo. Glymo is a precursor that is currently used for abrasion resistant coatings in the ophthalmic industry. A high crosslinking rate is achieved, but its refractive index is limited to 1.51. Higher refractive index coatings are obtained by adding high refractive index nanoparticles, such as TiO_2 or ZrO_2. Such coatings are limited in refractive index due to the low RI of the Glymo. When the content of high RI nanoparticles is increased the coatings becomes brittle and mechanical performance is reduced.

Accordingly, it is an object of the present invention to provide a new class of materials, and their applications as high refractive index bulk materials and coatings.

For the process embodiment of the invention, we propose:

(i) mixing a polythiol (I) and an alkenyl silane (II), to obtain or make a solution; and

(ii) exposing the solution to UV radiation or heat, preferably by UV radiation, to undergo thiol-ene addition thereby producing a polysulfide polysilane (III).

The mixing step (i) may comprise the addition before, during or after the mixing, of a further compound, which may be, for example, a catalyst, a photoinitiator, a solvent or combinations thereof. The photoinitiator is particularly useful for carrying out the further step (ii) by exposing the solution to UV radiation. The catalyst is particularly useful for carrying out the further step (ii) by exposing the solution to heat.

The polythiol (I) has a formula,

$(HS)\text{-}R\text{-}(SH)_n$,

wherein

- n is an integer comprised from 1 to 5 inclusive; and

- R is a group selected from:

arylene,

heteroarylene,

and linear or branched ($C_2 - C_{30}$) alkylene, wherein from 1 to 10 carbon atoms may be replaced by a group selected from (CO), (SO_2), NR_4 where R_4 represents a hydrogen atom or linear or branched (C_1-C_6) alkyl, O, S, or P; and/or each alkylene group may be optionally substituted by a group selected from hydroxyl, carboxy, aryl, and heteroaryl, these two last groups may be substituted onto the said alkylene chain at a terminal position or inside the alkylene chain.

The alkenyl silane (II) has the formula

$(R_1)_mX_{(3-m)}Si\text{-}R_2\text{-}R_3$

wherein:

- R_1 is a linear or branched (C_1–C_{10}) alkyl group, which comprised optionally from 1 to 5 heteroatoms selected from NR_6 where R_6 represents a hydrogen atom or linear or branched (C_1-C_6) alkyl, O, S, or P; and/or each alkyl group may be optionally substituted by a group selected from hydroxyl, carboxy, and (C_1-C_6) alkoxy;

- X is a group selected from a halogen atom, and $-OR_5$, wherein R_5 represents a group selected from (C_3-C_{10}) cycloalkyl, (C_3-C_{10}) heterocycloalkyl, and linear or branched (C_1-C_6) alkyl which may be comprised from 1 to 3 heteroatoms selected from the group consisting of NR_7 where R_7 represents a hydrogen atom or linear or branched (C_1-C_6) alkyl, O or S; and/or each alkyl group may be substituted by a group selected from linear or branched (C_1-C_6) alkoxy, carboxy, and hydroxy;

- m is an integer comprised from 0 to 2 inclusive;

- R_2 is either absent or represented by a group selected from linear or branched (C_2-C_{10}) alkylene wherein from 1 to 4 carbon atom may be replaced by a group selected from (CO), NR_8, where R_8 represents a hydrogen atom or linear or branched (C_1-C_6) alkyl, O or S; and/or each alkylene group may be optionally substituted by a group selected from linear or branched (C_1-C_6) alkoxy, carboxy, and hydroxy;

- R_3 represents a group selected from linear or branched (C_2-C_{10}) alkenyl, (C_4-C_{10}) cycloalkenyl, and (C_4-C_{10}) heterocycloalkenyl, each of these groups may be optionally substituted by a group selected from linear or branched (C_1-C_6) alkyl, linear or branched (C_1-C_6) alkoxy, linear or branched (C_1-C_6) thioalkoxy, carboxy, thiol, and hydroxyl.

In the present application the following definitions apply:

Aryl means monocyclic or polycyclic aromatic group which comprise usually from 4 to 14 carbon atoms and is optionally substituted by a group selected from hydroxy, linear or branched (C_1-C_6) alkyl, linear or branched (C_1-C_6) alkoxy, and carboxy. In accord with this meaning, the following aryl group could be mentioned, for example, phenyl, naphtyl, acenaphtenyl, biphenylenyl, anthracyl. According to the invention, the preferred aryl group represents a phenyl group.

Arylene means monocyclic or polycyclic aromatic group which comprise usually from 4 to 14 carbon atoms and an unsaturated double bond.

Heteroaryl means an aryl group as defined hereinbefore and wherein at least one carbon atom, and preferentially from 1 to 4 carbon atom, of the monocyclic or polycyclic is replaced by an heteroatom selected from O, N, and S. In accord with this meaning the following heteroaryl could be mentioned, for example, pyrymidyl, furyle, thienyl, thiadiazolyl, oxadiazolyl.

Halogen atom means an atom selected from Cl, Br, F and I.

Heteroarylene means an aryl group as defined hereinbefore and wherein at least one carbon atom, and preferentially from 1 to 4 carbon atom, of the monocyclic or polycyclic is replaced by an heteroatom selected from O, N, and S.

Alkylene means alkyl group which comprises an unsaturated double bond.

Alkenyl means alkyl group which comprises an unsaturated triple bond.

In the definition of compounds of formula (I) and (II), when it is mentioned that a group may be "substituted", it may be understood that in preferred embodiments such a group comprises from 1 to 4 substituents.

The synthesized polysulfide polysilanes (III), obtained by thiol-ene addition, possesses generally a refractive index in the range comprises from 1.47 to 1.55.

For the product embodiment of the invention, we propose a polysulfide polysilane for the elaboration of high refractive index materials, said polysulfide polysilane being synthesized as the reaction product of a polythiol (I) and an alkenyl silane (II).

These and other aspects, features and advantages of the present invention will be described or become apparent from the following detailed description of preferred embodiments.

As an overview of the new compound, a polythiol reactant is combined with an alkenylsilane reactant to provide a high index precursor material, which we refer to as polysulfide polysilane. The polysulfide polysilane is characterized by its preparation process. However the invention encompasses also the polysulfide polysilane of the invention if prepared by another preparation process. Thus the polysulfide polysilane is obtainable by the process according to the invention, and preferably is obtained by said process.

The polythiol (I) may be selected from the following, usually commercially available, compounds: 1,2-ethanedithiol; 1,3-propanedithiol; 1,4-butanedithiol; 1,2-butanedithiol; 1,5-pentanedithiol; 1,6-hexanedithiol; 1,8-

octanedithiol; 2,2'-oxydiethanethiol; 3,6-dioxa-1,8-octanedithiol; ethylene glycol bisthiol-glycolate; dl-1,4-dithiothreitol; 2,2'-thiodiethanethiol; bis(2-mercaptoethyl)sulphone; 2,5-dimercapto-1,3,4-thiadiazole; 5-({2-[(5-mercapto-1,3,4-thiadiazol-2-yl)thio]ethyl}thio)-1,3,4-thiadiazole-2-thiol; pentaerythritol tetra(2-mercaptoacetate); trimethylolpropane tris (3-mercaptopropionate); trimethylolpropane tris (2-mercaptoacetate); 1,4-benzenedithiol; 1,3-benzenedithiol; 3,4-dimercaptotoluene; 1,4-benzenedimethanethiol; 1,3-benzenedimethanethiol; 1,6-di(methanethiol)-3,4-dimethyl-phenyl; [3-(mercaptomethyl)-2,4,6-trimethylphenyl]methanethiol; 1,5-dimercaptonaphthalene; 3,3'-thiobis[2-[(2-mercaptoethyl)thio]-1-propanethiol; 5-[3-(5-mercapto-1,3,4-oxadiazol-2-yl)propyl]-1,3,4-oxadiazole-2-thiol; 2-mercaptoethyl sulfide; 1,3,5-triazine-2,4,6(1H, 3H, 5H)-trithione; and 2,3-bis[(2-mercaptoethyl)thio]-1-propanethiol; preferably selected from the group comprising trimethylolpropane tris (2-mercaptoacetate), 2-mercaptoethyl sulfide, 3,6-dioxa-1, 8-octanedithiol, ethylene glycol bisthiol-glycolate, 3,3'-thiobis[2-[(2-mercaptoethyl)thio]-1-propanethiol and trimethylolpropane tris (3-mercaptopropionate), and more preferably selected from the group comprising 3,3'-thiobis[2-[(2-mercaptoethyl)thio]-1-propanethiol and trimethylolpropane tris (2-mercaptoacetate).

More generally, preferred polythiols will be those that can be formed into polysulfide polysilanes having a high refractive index (RI), for example, those resulting in an RI of about 1.47 or greater, and more preferably above 1.55. Exemplary polythiols which produce generally such RI values are trimethylolpropane tris (2-mercaptoacetate), 2-mercaptoethyl sulfide, 3,6-dioxa-1, 8-octanedithiol, ethylene glycol bisthiol-glycolate, 3,3'-thiobis[2-[(2-mercaptoethyl)thio]-1-propanethiol and trimethylolpropane tris (3-mercaptopropionate).

In practical tests described in greater detail below, 3,3'-thiobis[2-[(2-mercaptoethyl)thio]-1-propanethiol and trimethylolpropane tris (2-mercaptoacetate) emerged as the most preferred polythiols.

The polythiols (I) preferably have from 2 to 4 thiol groups (inclusive).

In the polythiols, R comprises preferentially from 1 to 20 carbon atoms, and when a heteroatom is present in the R group, it is preferentially a sulfur atom. In a first embodiment of the polythiol, R comprises preferentially from 1 to 10 carbon atoms, and from 1 to 6 sulfur atoms. Then in a further embodiment, the compound of formula (I) has a high ratio of S atoms to C atoms (nS/nC) that is to say at least 1 over 4 (nS/nC =1/4). This means that in the preferred compound of formula (I), there is at least 1 sulfur atom for 4 carbon atoms. The compound of formula (I) has more preferably a ratio of S atoms to C atoms (nS/nC) of at least 1 over 2 and even more preferably a ratio of at least 7 over10.

In a non limiting embodiment, the alkenyl silane (II) is selected from the group comprising vinylphenylmethymethoxysilane, vinylphenylmethylchlorosilane , vinylphenyldiethoxysilane , vinylphenyldichlorosilane , 10-undecenyltrimethoxysilane , 10-undecenyltrichlorosilane, 10-undecenyldimethylchlorosilane , 7-octenyltrimethoxysilane , 7-octenyltrichlorosilane , 7-octenyldimethylchlorosilane , allyltrimethoxysilane , allyltriethoxysilane , allyltrichlorosilane , allylphenyldichlorosilane , allyloxyundecyltrimethoxysilane , allylmethyldichlorosilane , allyldimethylchlorosilane, allyldimethoxysilane , allyldichlorosilane , allyl(chloropropyl)dichlorosilane , allyl(chloromethyl)dimethylsilane , 3- (n-allylamino)propyltrimethoxysilane , butenyltriethoxysilane , butenylmethyldichlorosilane , 5-hexenyltrichlorosilane , 5-hexenyldimethylchlorosilane , hexenyltriethoxysilane , vinyltriisopropoxysilane , vinyltris(methoxypropoxy)silane , vinyltris(2-methoxyethoxy)silane , vinyltriphenoxysilane , vinyltrimethoxysilane , vinyltriethoxysilane , vinyltrichlorosilane, vinyltri-t-butoxysilane , vinyltriacetoxysilane , vinyloctyldichlorosilane , vinylmethyldimethoxysilane , vinylmethyldiethoxysilane , vinylmethyldichlorosilane , vinylmethyldiacetoxysilane , 3-cyclohexenyltrichlorosilane , [2-(3-cyclohexenyl)ethyl]triethoxysilane , 3-(trimethoxysilyl)propyl methacrylate, and preferably vinyltrimethoxysilane.

Preferred alkenyl silanes will be those that can form into polysulfide polysilanes having a high refractive (RI) index, for example, those resulting in an RI of about 1.47 or greater, and more preferably above 1.5. In a practical test described in greater detail below, vinyltrimethoxysilane emerged as a preferred silane since it provided a polysulfide polysilane having an RI of 1.509.

A preferred form of the alkenyl silane is where m is zero, X is an alkoxy group, and R_2 is absent or represents a (C_2-C_3) alkylene group.

The thiol-ene addition reaction may be carried out upon stoichiometric quantities of the reactants. Non-stoichiometric quantities can be employed. In general, excess quantities of alkenyl silane (II) may be utilized to maximize the yield of the thiol-ene addition. When an excess of alkenyl silane is used for the thiol-ene addition, the product of the reaction may be purified or the reaction mixture used as is for hydrolysis.

An hydrolysis step addition may be performed according to the invention, either in a separate stage from the one or more thiol-ene addition stage reactions or in a single stage together with the thiol-ene addition, in a so-called “one pot reaction.” The hydrolysis provides according to the invention a hydrolyzed product or a mixture of hydrolyzed compounds.

The thiol-ene addition can be carried out under normal atmospheric conditions, while an inert atmosphere is preferred. The thiol-ene addition can be carried out at room temperature (usually around 20 °C). Certain additions are exothermic, and it may be preferable to cool the solution.

Those skilled in the art are aware that the thiol-ene reaction can be initiated by one of several techniques. To facilitate the reaction, one may add a photoinitiator. Among conventional photoinitiators the following can be used: benzophenones, acetophenone derivatives like α-hydroxyalkylphenylketones, benzoin alkyl ethers, benzylketals, monoacylphosphine oxides, bisacylphosphine oxides. When used the photoinitiators are present in a low amount such as lower that 1 weight % of the solution, preferably lower than 0.05% and even more preferably lower than 0.02%. If the photoinitiator can increase the rate of reaction, it also tends to increase yellowing of the composition and thus leads to the need of purification after synthesis of the polysulfide polysilane. Thus preferably the thiol-ene reaction is conducted without any photoinitiator.

In some specific cases a solvent might optionally be used. In such cases the solvent used generally does not interact with the thiol-ene addition. The solvent is preferably a non protic solvent. Solvents comprising insaturations like carbon double bonds should generally be avoided. A solvent can be used when the two reactants (I) and (II) are not miscible and/or when one of these two reactants is solid at the temperature at which the reaction is taking place. An example of solvent which might be used optionally is tetrahydrofuran.

Accordingly, the invention also concerns a process for completely or partially hydrolyzing the polysulfide polysilane (III). This optionally includes hydrolyzing a blend of the polysulfide polysilane (III) with another different polysulfide polysilane (III) or other silane, preferably another different polysulfide polysilane (III), usually in the presence of an acidic aqueous solution or a basic aqueous solution. The use of an acidic aqueous solution is preferred for the hydrolysis, in order to better control and separate the hydrolysis and the condensation steps. This acidic solution may be an acidic water solution (HCl in H_2O). The resulting products from hydrolyzing with the various options discussed are also part of the present invention.

COATINGS – The polysulfide polysilane (III) can be hydrolyzed to form an optical coating. Prior to hydrolyzing, another polysulfide polysilane or silane such as Glymo may be mixed with said polysulfide polysilane (III).

Thus the invention also concerns a process as already described, wherein following the exposing step (ii), the process further comprises the step (iiia) of hydrolyzing the polysulfide polysilane (III), said hydrolysis being preferentially an acidic hydrolysis, for example an hydrolysis in the presence of HCl, to form an optical coating (IVa).

Thus the invention further concerns a process as already described, wherein following the exposing step (ii), the process further comprises the steps of:

mixing the polysulfide polysilane (III) with another silane selected from the group consisting of Glymo, another different polysulfide polysilane (III) and combinations thereof; and

hydrolyzing (iiib) the mixture to form an optical coating (IVb), said hydrolysis being preferentially an acidic hydrolysis.

Thus the hydrolyzed products of the invention with the optional addition of silanes such as Glymo before the hydrolysis or the optional addition of inorganic nanoparticles can form high refractive index coatings.

The hydrolysis and the coating manufacture is well known form the one skilled in the art, and is for example described in US 6 624 237. The process according to the invention can further comprise the step of adding nanoparticles made from inorganic oxide(s) to the optical coating (IVa) or (IVb), wherein the nanoparticles are comprised preferably from 20% to 80% of the weight of the optical coating (IVa) or (IVb). This results generally in an optical coating having a refractive index in the range from 1.59 to 1.67, or greater.

For example, after hydrolyzing, a colloid may be added. This colloid is used as a source of nanoparticles and may include an inorganic oxide selected from the group consisting of silicon dioxide (silica), aluminum oxide (alumina), antimony oxide, tin oxide, titanium oxide, zirconium oxide and mixtures of such inorganic oxides. The hydrolyzed material comprising nanoparticles may be used as a high index hard coat for optical products, such as lenses.

The inorganic oxide which constitutes the nanoparticles is preferably added to the hydrolyzed product in the form of a colloid. It is preferable that the inorganic oxide maintains a stable dispersion state in the matrix and/or a low haze level, therefore, the average size of such particles may range from 1 to 200 nanometers, preferably from 2 to 100 nanometers, and more preferably, from 5 to 50 nanometers.

Examples of the above inorganic oxide include SiO_2, Al_2O_3, SnO_2, Sb_2O_5, Ta_2O_5, CeO_2, La_2O_3, Fe_2O_3, ZnO, WO_3, ZrO_2, In_2O_3 and TiO_2 alone or by mixture of at least two of them.

The inorganic oxides have a refractive index of from 1.7 to 3.0, and more preferably may be a multi-component oxide(s) including two or more compounds selected from the group consisting of TiO_2 (refractive index: 2.5-2.7), SiO_2 (refractive index: 1.5), ZrO_2 (refractive index: 2.2), SnO_2 (refractive index: 2.0),

Ce_2O_3 (refractive index: 2.2), $BaTiO_3$ (refractive index: 2.4), Al_2O_3 (refractive index: 1.73), and Y_2O_3 (refractive index: 1.92). Said multi-component oxide(s) may be composed at adequate contents by their refractive index, and more preferably, at least one of TiO_2-ZrO_2-SnO_2, TiO_2-ZrO_2-SiO_2 and TiO_2-SnO_2-SiO_2 may be used. Preferred the multi-component oxide according to the invention is selected from the group consisting of Optolake 1120z(S-95-A8)® and Optolake 1130Z(S-7-A8)®, which both are TiO_2-ZrO_2-SiO_2 composites with core-shell structure.

The process includes preferably adding colloids in the form of nanoparticles of inorganic oxide(s) after the hydrolysis step. The resulting hydrolyzed coatings may include one or more polysulfide polysilane made according the invention; may include Glymo or other silanes; and may include colloids. A catalyst or a solvent can optionally be added to the coating. The applications include dip-coating, spin-coating, flow, fan-coating, spray coating and other lens coating techniques. Dip-coating and spin-coating are industrially cost effective and are the preferred techniques. After the coating is applied to a precursor of a lens (or lens substrate material), it is cured and crosslinked to form a solid, hard coat.

The coating may be applied to a wide variety of lens substrate materials (or substrates). The substrates may be selected from mineral glass and also organic glass made of, for example, polycarbonate, polyamide, polyimide, polysulfone, copolymers of polyethyleneterephthalate and polycarbonate, polyolefine, homopolymers and copolymers of diethylene glycol bis(allylcarbonate), homopolymers and copolymers of (meth)acrylic monomers, homopolymers and copolymers of thio(meth)acrylic monomers, homopolymers and copolymers of urethane, homopolymers and copolymers of thiourethane, epoxy homopolymers and copolymers, and episulfure homopolymers and copolymers.

Preferably, the substrate is an organic material, more preferably it is an organic lens. According to a preferred embodiment of the invention, the substrate is an optic glass or an optical lens which is selected from ophthalmic lens, ocular visor, and sight optical systems. In a preferred embodiment, the substrate is an ophthalmic lens which may be an afocal, a unifocal, a bifocal, a trifocal or a progressive lens. Each ophthalmic lens may be also transparent, solar, or photochromic. In such case, the substrate coated with the abrasion-resistant coating may be overcoated with classical properties enhancing coatings such as anti-reflecting coating and top coat. Anti-reflecting coatings and their methods of making are well known in the art. The top coat, typically a hydrophobic top coat, which in the finished optical article constitutes the outermost coating on the optical substrate, is intended for improving the dirty mark resistance of the finished optical article.

Preferred substrates according to the invention are transparent substrates having a refractive index not smaller than 1.50 and include, for example, those made of polycarbonates which have a refractive index of 1.50. Moreover, a number of resins have been proposed in many patent publications and laid-open applications for use as plastic lenses for glasses, including those lenses made of polyurethane resins, methacrylic polymers, acrylic polymers and combinations thereof. For instance, lenses made of urethane resins are ones which are obtained by thermally curing monomers MR-6, MR-7 and MR-8 (commercially available from Mitsui Toatsu Chemicals Inc.). Lenses made of methacrylic polymers are those obtained by radical polymerization of TS-26 monomer commercially available from Tokuyama Co., Ltd.). Likewise, lenses obtained by use of urethane reaction and vinyl polymerization are those obtained by polymerizing ML-3 monomer (commercially available from Mitsubishi Gas Chemical Co., Inc.). All these resins can be used as substrates.

The coating can be applied to either the convex surface or the concave surface of the lens, or both. The hard coat should preferably have a dry final thickness of from about 0.2 microns (µm) to about 10 microns (µm). The lens may be treated or contacted with a primer prior to application of the coating layer.

BULK MATERIALS – The inventions also concerns a process as described above, wherein following the exposing step (ii), the process further comprises the steps of:

- hydrolyzing (iv) the polysulfide polysilane (III); and

- concentrating and then heating the hydrolyzed material to form a bulk material (V).

More generally, the polysulfide polysilane (III) of the invention is transformed into a bulk material (or lens substrate material or substrate) in a process known by the one skilled in the art, and said bulk material is encompassed by the invention.

In a preferred embodiment, following said hydrolyzing step (iv), the process further comprises the step of adding a catalyst selected from the group comprising metal chelates and amines.

To form bulk materials, the hydrolyzed product is preferably subjected to a sol-gel process including evaporation and crosslinking during a carefully controlled heating step leading to a densified and transparent material suitable fo use as bulk materiall (or substrate for lens substrate material), for example as described in US Patent 6,624,237. In general for the one skilled in the art "concentration" has the same meaning than "evaporation". A typical method for fabricating transparent dense glasses based on silanes using the sol-gel route, may comprise the following steps: A) a complete hydrolysis of a solution containing one or a several silicon alkoxides is carried out in a solvent or a mixture of organic solvents of the alkoxide(s) by using an aqueous acidic solution; B) the organic solvent(s) and the residual alcohols are removed, and the resulting solution is concentrated by distillation under primary vacuum conditions so as to obtain a viscous sol, having for example a concentration of 1-10 moles/l in silicon atoms; C) gelling and air drying or drying in an inert atmosphere are initiated at a temperature lower than 158° F (70° C); D) the glass may be annealed at a temperature lower than 932° F (500° C).

The bulk material manufacture is well known by the one skilled in the art, and is for example described in US 6,624,237.

As used in the present specification, the term sol means and includes a colloidal dispersion of finely divided solid inorganic inorganic oxide particles in an aqueous or an organic liquid.

In one embodiment, the sol is slowly evaporated at room temperature and atmospheric pressure for 2 hours (h) to several weeks, preferentially for 15h. Optionally the partial evaporation is conducted under reduced pressure. In another embodiment the sol or the gel is heated at a temperature between 104° F and 392° F (40°C and 200°C), preferentially between 104° F and 266° F (70°C and 130°C) for a time comprised between 30 minutes and 3 weeks, preferentially between 4h and 72h. Optionally a condensation catalyst is added to the hydrolyzed compound in order to accelerate the crosslinking process.

The RI of the bulk materials according to the invention is generally in the range of at least 1.6, and preferably at least 1.63. This bulk material is generally characterized by a high refractive index, excellent transparency and low density.

The invention also encompasses a polysulfide polysilane (III) obtainable by a process as disclosed above, and having preferably a refractive index in the range of 1.47 to 1.55.

The invention also encompasses an optical coating (IVa, IVb) obtained by hydrolyzing said polysulfide polysilane (III), preferably wherein the optical coating (IVa, IVb) includes nanoparticles made from inorganic oxide(s), preferably in the range of between 20% and 80% of the weight of the optical coating (IVa, IVb).

The invention also encompasses an optical article, preferably an optical lens, made from a lens substrate material and coated by said optical coating.

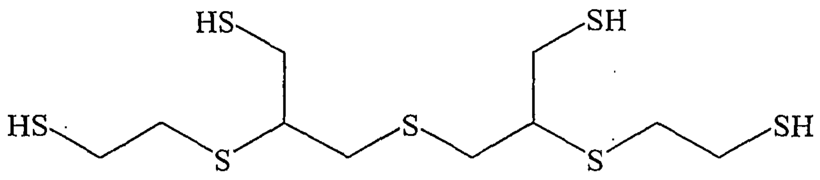
The invention also encompasses a bulk material (V) obtained by hydrolyzing, concentrating and then heating said polysulfide polysilane (III).

The invention also encompasses an optical article, preferably an optical lens, made from said bulk material (V).

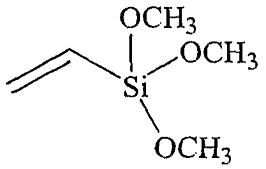
The process according to the invention will now be discussed in greater detail, by reference to the following examples.

Example 1

3,3'-thiobis[2-[(2-mercaptoethyl)thio]-1-Propanethiol (MR10B) and vinyltrimethoxysilane (VTMOS) were mixed together with tetrahydrofuran (THF) solvent to allow initial miscibility.

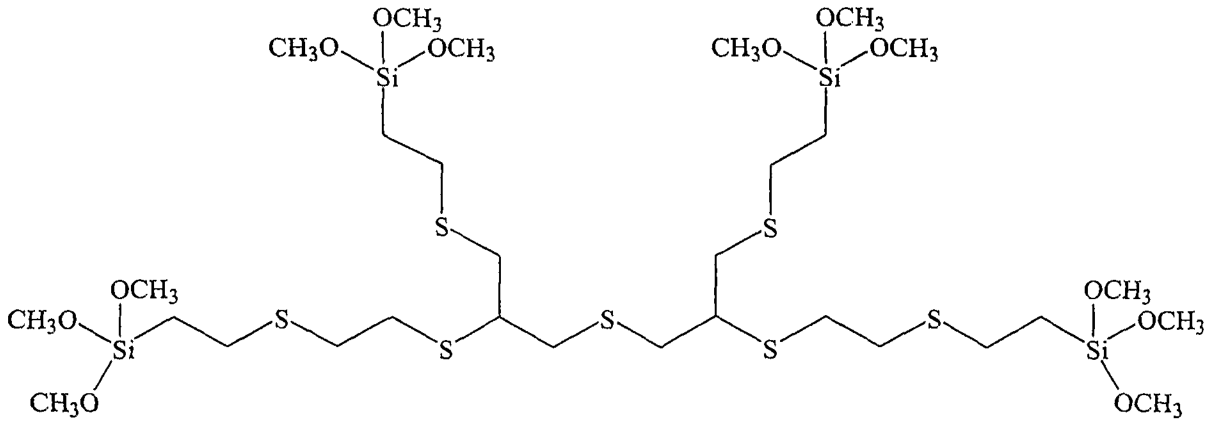


3,3'-thiobis[2-[(2-mercaptoethyl)thio]-1-Propanethiol



vinyltrimethoxysilane

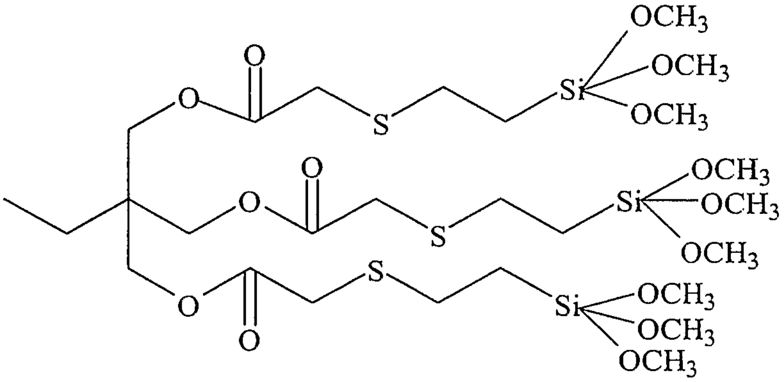
The solution was placed in a vial and exposed to UV irradiation. This represented one stoichiometric quantity of 3,3'-thiobis[2-[(2-mercaptoethyl)thio]-1-propanethiol, or MR10B, and four stoichiometric quantities of vinyltrimethoxysilane, or VTMOS. The thiol-ene addition took place under UV, without addition of any catalyst. The reaction product was as follows:



By weight, 13.23g MR10B, 12.45g VTMOS, and 4.32g THF were combined in a glass vial to produce approximately 30 grams of solution. The irradiation step consisted of five passes under the Fusion UV source (H Bulb), by a conveyor belt at 4.95 cm/s. The resulting polysulfide polysilane had a refractive index of 1.546.

Example 2

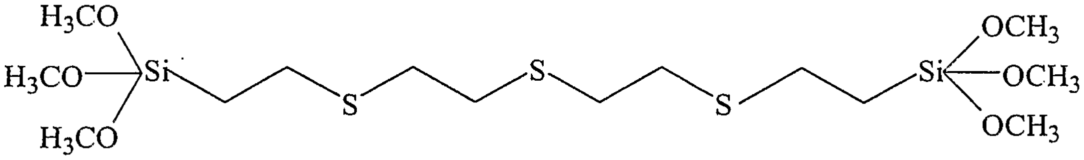
By weight, 35.65 g of trimethylolpropane tris (2-mercaptoacetate) and 44.47 g vinyltrimethoxysilane (VTMOS) were mixed together and subjected to UV radiation consisting of 5 passes under the Fusion UV source (H Bulb), on a conveyor belt at 4.95cm/s. The UV dose was 10.13 J/cm^2 at an intensity of 3.401 Watts/cm^2. A solvent was not necessary for miscibility of the VTMOS, but it could be optionally used. The resulting structure was:



The polysulfide polysilane produced had a refractive index of 1.477.

Example 3

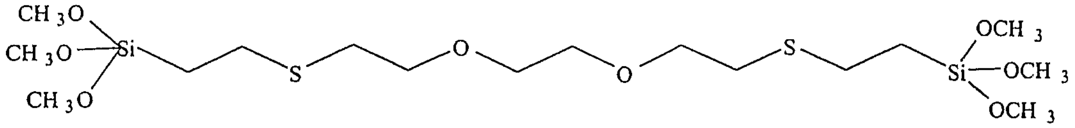
Under conditions similar to Example 2, 10 g of 2-Mercaptoethyl Sulfide was combined with 19.22 g of VTMOS to produce the following compound:



The compound had a refractive index of 1.509.

Example 4

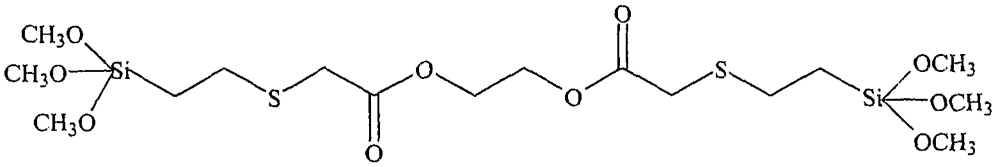
Under conditions similar to Example 2, 10 g of 3,6-Dioxa-1, 8-Octanedithiol was combined with 16.27 g of VTMOS to produce the following compound:



The compound had a refractive index of 1.460.

Example 5

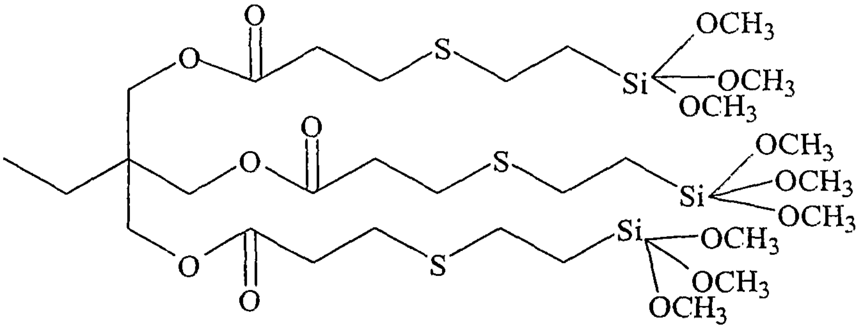
Under conditions similar to Example 2, 30 g of Ethylene Glycol Bisthiolglycolate was combined with 42.23 g of VTMOS to produce the following compound:



The compound had a refractive index of 1.475.

Example 6

Under conditions similar to Example 2, 35.65 g of Trimethylolpropane tris (3-mercaptopropionate) was combined with 49.72 g of VTMOS to produce the following compound:



The compound had a refractive index of 1.480.

Example 7

The product obtained in Example 1 was hydrolyzed by acidic water solution (HCl in H_2O 1N). The sol-gel process took place under controlled conditions followed by a heating step, leading to a transparent material. The 2 steps cross-linking stage was made of a 1st step of 15h at room temperature followed by 3 days at 212° F (100°C). The bulk material obtained presented a refractive index equal to 1.63 and an Abbe value of 41. These 2 optical characteristics were measured by ellipsometry and by brewster angle definition (Metricon) at several wavelength of the visible. The density of this material was

1.38. Accordingly, high refractive index bulk hybrid organic-inorganic material could be formed by hydrolyzing heating the various polysulfide polysilanes to create a highly-crosslinked matrix. The resulting matrix was suitable for use in optical applications, for example lenses, for ophthalmic use.

The various polysulfide polysilanes obtained in the examples 1 to 6 were hydrolyzed to create coating formulations. The following examples were prepared with various types of colloidal nanoparticles oxides.

Coating Example 8

The formulation of a coating was made as follows: 20.64 grams of precursor 2 were mixed with 41.21 grams of methanol and stirred till the mixture became clear. 4.6 grams of HCl/H_2O (0.1N) were then added over 1 minute while stirring. Once the solution cleared 21.0 grams of methanol were immediately added. 29.3 grams of the colloid Optolake 1130Z(S-7-A8)® from Catalysts & Chemicals Ind. Co., Ltd. were then slowly added, followed by 3.24 grams of methylethylketone. Finally, 0.01 grams of the surfactant EFKA 3034 were added to the solution.

Coating Examples 9-13

The formulation was the same as in example 8, but the polysulfide polysilane and the colloid were changed according to Table 1. Each coating is formulated based on 70% by weight of polysulfide polysilane before hydrolysis and 30% by weight of nanoparticles colloid from Catalyst & Chemicals Ind. Co., Ltd (excluding the dispersion medium of the colloid).

The coating solution was then deposited on lenses made from MR-8 (commercially available from Mitsui Toatsu Chemicals Inc.) by spin coating (for about 5 seconds at 500 rpm followed by 10s at 750 rpm). Once deposited on a lens the coating was cured at 212° F (100°C) for 3 hours.

Each coating is characterized, as reported in Table 1, by the refractive index of the matrix (cured in the same conditon) without colloid (column 5) and by the refractive index of the coating based on the polysulfide polysilane and the nanoparticles (column 6).

It should be understood that any combination of polysulfide polysilanes and colloids can be used together, and that Table 1 simply provides a limited number of exemplary combinations.

Example	Example of polysulfide polysilane	TiO_2 based High Refractive Index Nanoparticles, from Catalyst & Chemicals Ind. Co., Ltd	RI of the polysulfide polysilane	RI of the matrix after hydrolysis-condensation	RI of a coating made of 70%wt matrix and 30%wt High Index Nanoparticles
8	2	1130Z(S-7-A8)	1.477	1.545	1.62
9	1	1120Z(11RU-7-A8)	1.546	1.630	1.67
10	3	1120Z(11RU-7-A8)	1.509	1.587	1.62
11	4	1120Z(11RU-7-A8)	1.460	1.538	1.59
12	5	1120Z(11RU-7-A8)	1.475	1.538	1.59
13	6	1120Z(11RU-7-A8)	1.480	1.552	1.60

Table 1

Coatings Examples 14 , 15

Coatings 14 and 15 were formulated the same way as the examples 8 to 13. As reported in Table 2, the polysulfide polysilane from example 2 was used and various colloids from different suppliers. When not specified the supplier was Catalyst & Chemicals Ind. Co., Ltd.

The coatings 8, 9, 14 and 15 were also characterized with the Bayer abrasion test. The ASTM Bayer Abrasion resistant measurement was determined by measuring the percent haze of a coated and uncoated lens, before and after testing on an oscillating sand abrader as in ASTM F 735-81. The abrader was oscillated for 300 cycles with approximately 500 g of aluminum oxide (Al_2O_3) ZF 152412 supplied by Specially Ceramic Grains. The haze was measured using a Pacific Scientific Hazemeter model XL-211. The ratio of the uncoated lens haze (final-initial) was a measure of the performance of the coating, with a higher ratio meaning a higher abrasion resistance.

Example	polysulfide polysilane from example	Refractive index (RI)		RI of Matrix + Nanoparticles	Colloid	Bayer abrasion test value
		polysulfide polysilanes	Matrix			
9	1	1.546	1.62	1.67	1120Z(11RU -7-A8))	**~1**
8	2	1.477	1.545	1.623	1130Z(S-7-A8)	**~2.25**
14	2	1.477	1.545	1.612	1120Z(S-95-A8)	**~2**
15	2	1.477	1.545	1.567	Novacentrix Al_2O_3	**~1.5**

Table 2

The various Examples demonstrated that the hydrolyzed polysulfide polysilane materials could be further combined with colloids to form a high refractive index coating, which was suitable for coating onto optical articles, for example lenses, for ophthalmic use. The coatings presented herein could be a full or partial replacement for Glymo where a higher refractive index was desired.

In general, the higher refractive index coating would provide at least the following benefits:

Use a lower amount of expensive high refractive index colloids;

Provide a RI above 1.5, preferably above 1.59 and even more preferably above 1.67;

Use lower refractive index and cheaper colloids for the same refractive index;

Decrease the haze because of the need of less nanoparticles to reach a given refractive index; and

Decrease the haze by lowering the refractive index contrast between matrix and high index nanoparticles.

In conclusion, there have been described and shown two classes of reactants which could be combined pursuant to the thiol-ene addition reaction, the resulting polysulfide polysilanes (III) being characterized an hybrid organic-inorganic material that is highly transparent. The hybrid material usually combines excellent optical properties, such as low haze, with good mechanical properties.

Although illustrative embodiments of the present invention have been described, it is to be understood that the present invention is not limited to those precise embodiments, and that various other changes and modifications may be affected therein by one skilled in the art without departing from the scope or spirit of the present invention.

CLAIMS

What is claimed is:

1. A process for synthesizing a polysulfide polysilane (III), comprising the steps of:

(i) Mixing:

1) - a polythiol (I) represented by the general formula,

$(HS)\text{-}R\text{-}(SH)_n$ (I)

wherein:

- n is an integer comprised from 1 to 5 inclusive; and

- R is a group selected from:

arylene

heteroarylene,

and linear or branched ($C_2 - C_{30}$) alkylene, wherein from 1 to 10 carbon atom may be replaced by a group selected from (CO), (SO_2), NR_4 where R_4 represents a hydrogen atom or linear or branched (C_1-C_6) alkyl, O, S, and P; and/or each alkylene group may be optionally substituted by a group selected from hydroxyl, carboxy, aryl, and heteroaryl; and

2) an alkenyl silane (II) represented by the general formula

$(R1)_mX_{(3-m)}Si\text{-}R_2\text{-}R_3$ (II)

wherein:

- R1 is a linear or branched (C_1–C_{10}) alkyl group, which comprises optionally from 1 to 5 heteroatoms selected from NR_6 where R_6 represents a hydrogen atom or linear or branched (C_1-C_6) alkyl, O, S, or P; and/or each alkyl group may be optionally substituted by a group selected from hydroxyl, carboxy, and (C_1-C_6) alkoxy;

- X is a group selected from a halogen atom, and $-OR_5$, wherein R_5 represents a group selected from (C_3-C_{10}) cycloalkyl, (C_3-C_{10}) heterocycloalkyl, and linear or branched (C_1-C_6) alkyl which may be comprised from 1 to 3 heteroatoms selected from the group consisting of NR_7 where R_7 represents a hydrogen atom or linear or branched (C_1-C_6) alkyl, O, S; and/or each alkyl group may be substituted by a group selected from linear or branched (C_1-C_6)alkoxy, carboxy, and hydroxy;

- m is an integer comprised from 0 to 2 inclusive;

- R_2 is either absent or represented by a group selected from linear or branched (C_2-C_{10}) alkylene wherein from 1 to 4 carbon atoms may be replaced by a group selected from (CO), NR_8 where R_8 represents a hydrogen atom or linear or branched (C_1-C_6) alkyl, O or S; and/or each alkylene may be optionally substituted by a group selected from linear or branched (C_1-C_6) alkoxy, carboxy, and hydroxy;

- R_3 represents a group selected from linear or branched (C_2-C_{10}) alkenyl, (C_4-C_{10}) cycloalkenyl, and (C_4-C_{10}) heterocycloalkenyl, each of these groups may be optionally substituted by a group selected from linear or branched (C_1-C_6) alkyl, linear or branched (C_1-C_6) alkoxy, linear or branched (C_1-C_6) thioalkoxy, carboxy, thiol, and hydroxyl;

to obtain a solution ; and

(ii) exposing the solution to UV radiation or heat, preferably by UV radiation, to undergo thiol-ene addition thereby producing a polysulfide polysilane (III).

2. A process according to claim 1, wherein the polythiol (I) includes 2 to 4 thiol groups.

3. A process according to one of claims 1 or 2, wherein in the polythiol (I), R comprises from 1 to 20 carbon atoms, and when a heteroatom is present in the R group, it is a sulfur atom.

4. A process according to one of the claims 1 to 3, wherein in the polythiol (I), the ratio of S atoms to C atoms (nS/nC) is at least 1 over 4 preferably at least 1 over 2 and more preferably at least 7 over 10.

5. A process according to one of claims 1 to 4, wherein the polythiol (I) is selected from the group comprising 1,2-ethanedithiol; 1,3-propanedithiol; 1,4-

butanedithiol; 1,2-butanedithiol; 1,5-pentanedithiol; 1,6-hexanedithiol; 1,8-octanedithiol; 2,2'-oxydiethanethiol; 3,6-dioxa-1,8-octanedithiol; ethylene glycol bisthiol-glycolate; dl-1,4-dithiothreitol; 2,2'-thiodiethanethiol; bis(2-mercaptoethyl)sulphone; 2,5-dimercapto-1,3,4-thiadiazole; 5-({2-[(5-mercapto-1,3,4-thiadiazol-2-yl)thio]ethyl}thio)-1,3,4-thiadiazole-2-thiol; pentaerythritol tetra(2-mercaptoacetate); trimethylolpropane tris (3-mercaptopropionate); trimethylolpropane tris (2-mercaptoacetate); 1,4-benzenedithiol; 1,3-benzenedithiol; 3,4-dimercaptotoluene; 1,4-benzenedimethanethiol; 1,3-benzenedimethanethiol; 1,6-di(methanethiol)-3,4-dimethyl-phenyl; [3-(mercaptomethyl)-2,4,6-trimethylphenyl]methanethiol; 1,5-dimercaptonaphthalene; 3,3'-thiobis[2-[(2-mercaptoethyl)thio]-1-propanethiol; 5-[3-(5-mercapto-1,3,4-oxadiazol-2-yl)propyl]-1,3,4-oxadiazole-2-thiol; 2-mercaptoethyl sulfide; 1,3,5-triazine-2,4,6(1H, 3H, 5H)-trithione; and 2,3-bis[(2-mercaptoethyl)thio]-1-propanethiol; preferably selected from the group comprising trimethylolpropane tris (2-mercaptoacetate), 2-mercaptoethyl sulfide, 3,6-dioxa-1, 8-octanedithiol, ethylene glycol bisthiol-glycolate, 3,3'-thiobis[2-[(2-mercaptoethyl)thio]-1-propanethiol and trimethylolpropane tris (3-mercaptopropionate), and more preferably selected from the group comprising 3,3'-thiobis[2-[(2-mercaptoethyl)thio]-1-propanethiol and trimethylolpropane tris (2-mercaptoacetate) .

6. A process according to one of claims 1 to 5, wherein in the alkenyl silane (II) m is zero, X is an alkoxy group, and R_2 is absent or represents a (C_2-C_3) alkylene group.

7. A process according to one of claims 1 to 6, wherein the alkenyl silane (II) is selected from the group comprising vinylphenylmethymethoxysilane, vinylphenylmethylchlorosilane , vinylphenyldiethoxysilane , vinylphenyldichlorosilane , 10-undecenyltrimethoxysilane , 10-undecenyltrichlorosilane, 10-undecenyldimethylchlorosilane , 7-octenyltrimethoxysilane , 7-octenyltrichlorosilane , 7-octenyldimethylchlorosilane , allyltrimethoxysilane , allyltriethoxysilane ,

allyltrichlorosilane, allylphenyldichlorosilane, allyloxyundecyltrimethoxysilane, allylmethyldichlorosilane, allyldimethylchlorosilane, allyldimethoxysilane, allyldichlorosilane, allyl(chloropropyl)dichlorosilane, allyl(chloromethyl)dimethylsilane, 3-(n-allylamino)propyltrimethoxysilane, butenyltriethoxysilane, butenylmethyldichlorosilane, 5-hexenyltrichlorosilane, 5-hexenyldimethylchlorosilane, hexenyltriethoxysilane, vinyltriisopropoxysilane, vinyltris(methoxypropoxy)silane, vinyltris(2-methoxyethoxy)silane, vinyltriphenoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane, vinyltrichlorosilane, vinyltri-t-butoxysilane, vinyltriacetoxysilane, vinyloctyldichlorosilane, vinylmethyldimethoxysilane, vinylmethyldiethoxysilane, vinylmethyldichlorosilane, vinylmethyldiacetoxysilane, 3-cyclohexenyltrichlorosilane, [2-(3-cyclohexenyl)ethyl]triethoxysilane, 3-(trimethoxysilyl)propyl methacrylate, and preferably vinyltrimethoxysilane.

8. A process according to one of claims 1 to 7, wherein following the exposing step (ii), the process further comprises the step (iiia) of hydrolyzing the polysulfide polysilane (III), said hydrolysis being preferentially an acidic hydrolysis, to form an optical coating (IVa).

9. A process according one of the claims 1 to 7, wherein following the exposing step (ii), the process further comprises the steps of:

mixing the polysulfide polysilane (III) with another silane selected from the group consisting of Glymo, another different polysulfide polysilane (III) and combinations thereof; and

hydrolyzing (iiib) the mixture to form an optical coating (IVb), said hydrolysis being preferentially an acidic hydrolysis.

10. A process according to one of claims 8 or 9, wherein following the hydrolyzing step (iiia) or (iiib), the process further comprises the step of adding nanoparticles made from inorganic oxide(s) to the optical coating (IVa) or (IVb),

wherein the nanoparticles are comprised preferably from 20% to 80% of the weight of the optical coating (IVa) or (IVb).

11. A process according one of claims 1 to 7, wherein following the exposing step (ii), the process further comprises the steps of:

hydrolyzing (iv) the polysulfide polysilane (III); and

concentrating and then heating the hydrolyzed material to form a bulk material (V).

12. A process according to the preceding claim, wherein following said hydrolyzing step (iv), the process further comprises the step of adding a catalyst selected from the group comprising metal chelates and amines.

13. A polysulfide polysilane (III) obtainable by a process according to one of claims 1 to 12, and having preferable a refractive index in the range of 1.47 to 1.55.

14. An optical coating (IVa, IVb) obtained by hydrolyzing the polysulfide polysilane (III) of claim 13, preferably wherein the optical coating (IVa, IVb) includes nanoparticles made from inorganic oxide(s), preferably in the range of between 20% and 80% of the weight of the optical coating (IVa, IVb).

15. A bulk material (V) obtained by hydrolyzing, concentrating and then heating the polysulfide polysilane (III) of claim 14.

16. An optical article, preferably an optical lens, made from a lens substrate material and coated by an optical coating according to claim 14.

17. An optical article, preferably an optical lens, made from the bulk material (V) according to claim 15.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2009/005574

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G75/04 C08L81/02

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

B. FIELDS SEARCHED

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

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 785 458 A (CATALYSTS & CHEM IND CO [JP]) 16 May 2007 (2007-05-16) paragraph [0021]; claim 1	1-17
A	US 4 366 307 A (SINGH HAKAM ET AL) 28 December 1982 (1982-12-28) column 9, lines 60-65; claim 1	1-17

☐ 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 18 August 2009	Date of mailing of the international search report 25/08/2009
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 Buestrich, Ralf

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2009/005574

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1785458 A	16-05-2007	CN 101010400 A JP 2006070144 A WO 2006025499 A1 US 2008268253 A1	01-08-2007 16-03-2006 09-03-2006 30-10-2008
US 4366307 A	28-12-1982	NONE	