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(54) Title: PROCESS FOR THE PRODUCTION OF ORGANOSILSESQUOXANES

(57) Abstract: A process for forming a composition comprising organosilsesquioxanes, comprises the following steps: 1. partially hydrolysing hydrolysable inorganic monomer precursors comprising at least 50 mole% of first hydrolysable inorganic monomer precursors having the formula $RSiY_3$, in which R is an organic group, the R-Si bond is a non-hydrolysable bond, each Y group is the same as or different to one another and is selected from chemically-reactive groups such that each Si-Y bond is hydrolysable to form a Si-OH bond, to form inorganic monomers and allowing partial condensation of the inorganic monomers to form a liquid composition comprising inorganic oligomers; 2. prior to complete condensation of the inorganic monomers, quenching the liquid composition with an amount of water which, in combination with the water used in step (1) and any water liberated by condensation of the inorganic monomers in step (1), is in excess of the stoichiometric amount of water required to achieve complete hydrolysis of all the hydrolysable inorganic monomer precursors present; and 3. drying the composition.

PROCESS FOR THE PRODUCTION OF ORGANOSILSESQUIOXANESField of the Invention

The present invention relates to a process for the production of organosilsesquioxanes, and to the use of a composition comprising organosilsesquioxanes to provide a protective coating on a substrate so as to impart to the substrate resistance to mechanical and chemical damage, while at the same time maintaining excellent optical properties, and as a bulk material.

Background to the Invention

Organosilsesquioxanes are silicon-oxygen based frameworks having the general formula $(\text{RSiO}_{1.5})_n$, in which n is an even number ≥ 4 . Organosilsesquioxanes which have a very specific structure, for example a compound having the formula $(\text{RSiO}_{1.5})_8$ has an octahedral cage structure, are referred to in the field as organooligosilsequioxanes or polyhedral oligomeric silsesquioxanes (or POSS®).

Organosilsesquioxanes have the potential to offer good mechanical properties, for example as coatings with good abrasion resistance, and can be formulated to have good chemical resistance, for instance as embodied by hydrolytic stability or stability to UV degradation. These and other properties render the organosilsesquioxanes useful as protective coatings for a wide variety of substrates, particularly polymer-based materials, such as acrylic polymers and polycarbonates, which are routinely used as alternatives to glass in many situations where the weight, tendency to shatter or expense of glass contraindicates its use.

A number of processes for the manufacture and modification of organosilsesquioxanes is described in the literature, including:

(1) the manufacture of partially or fully condensed structures;

(2) the functionalisation of partially or fully condensed structures; and

(3) the manufacture of structures containing more than one organic functionality.

Examples of such processes are disclosed by Brown *et al*, J. Am. Chem. Soc. (1965) 87:4313-4317 and Feher *et al*, J. Am. Chem. Soc. (1989) 111:1741-1748. In general terms, these processes the use of very low monomer concentrations in solvent and the addition thereto of large amounts of water, to allow the very slow production, typically over a number of months, of specific and defined cage structures. As a result, the materials produced have limited application, for instance in the field of protective coatings, due to the considerable expense associated with their slow production.

The incorporation of functional organic ligands into the basic organosilsesquioxane structure has been achieved through a number of routes. In this context, the term "functional" is used to describe organic groups that act to impart particular mechanical and/or chemical properties to the final material. For example, the incorporation of organic ligands has been achieved by:

(1) exchange of functionality in an existing fully condensed structure;

(2) cleavage and insertion of functionality into a fully condensed structure;

(3) addition of functionality into a partially condensed structure; and

(4) incorporation of functionality during the fabrication of the structure.

Examples of these processes are described in US-A-5047492 and US-A-5484867.

The last of the above routes, (4), is rarely performed, but where it is it involves co-hydrolysis and condensation of silane precursors containing non-functional

organic groups and silane precursors containing functional organic groups particularly with the ability to polymerise. However, the preparation of these functionalised organosilsesquioxanes remains slow.

It would, therefore, be desirable to provide a process for the preparation of organosilsesquioxanes, and compositions comprising the same, which is not subject to the lengthy reaction times described in the prior art, and which therefore makes these materials available to the industry on a more cost-effective basis.

Summary of the Invention

According to a first aspect of the present invention, a process for preparing a composition comprising organosilsesquioxanes comprising the following steps:

(1) partially hydrolysing hydrolysable inorganic monomer precursors comprising at least 50 mole% of first hydrolysable inorganic monomer precursors having the formula RSiY_3 , in which R is an organic group, the R-Si bond is a non-hydrolysable bond, each Y group is the same as or different to each other Y group and is selected from chemically-reactive groups such that each Si-Y bond is hydrolysable to form a Si-OH bond, to form inorganic monomers, and allowing partial condensation of the inorganic monomers to form a liquid composition comprising inorganic oligomers;

(2) prior to complete condensation of the inorganic monomers, quenching the liquid composition with an amount of water which, in combination with the water used in step (1) and any water liberated by condensation of the inorganic monomers in step (1), is in excess of the stoichiometric amount of water required to achieve complete hydrolysis of all the hydrolysable inorganic monomer precursors present; and

(3) drying the composition.

The process of the present invention allows for the controlled and rapid manufacture of a wide variety of organosilsesquioxane-based compositions. The compositions may comprise organosilsesquioxanes having one or more organic functionalities and/or having completely or incompletely condensed structures. Furthermore, the compositions may or may not comprise only organo-oligosilsesquioxanes.

According to a second aspect of the present invention, composition comprising organosilsesquioxanes are obtainable by the above-described process.

Other aspects of the present invention include the application of the above-described compositions to a variety of substrates, the coated substrates themselves, articles made from the above-described compositions, and use of the above-described compositions as bonding agents.

The compositions of the present invention are capable of providing coatings that confer abrasion resistance, hydrolytic stability and stability to UV degradation to a wide variety of substrates, particularly plastics substrates, and can be fine tuned to have other properties depending upon the nature of the functionalities incorporated therein and the conditions utilised in their preparation.

Detailed Description of the Invention

In general terms, the process of the present invention involves a two-step hydrolysis/condensation reaction and subsequent drying, and optionally curing, of the resulting composition. In the first step, hydrolysable inorganic monomer precursors, of which at least 50 mole% have the formula $RSiY_3$ (referred to as "first" hydrolysable monomer precursors"), are partially hydrolysed and allowed to undergo some condensation, but not complete condensation, to form inorganic oligomers that will form the building blocks for the final organosilsesquioxane molecules.

In the second step of the process, the inorganic oligomers are quenched by addition to, or addition thereto, of a relatively large amount of water, which has the effect of causing rapid condensation of the inorganic oligomers. Depending on the time allowed and the conditions used for condensation the degree of condensation may vary somewhat, up to essentially complete condensation of those oligomers.

The precise nature of the final structures formed on drying, and optionally curing, the composition produced is a matter for conjecture, but is not important given the beneficial mechanical and chemical properties achieved.

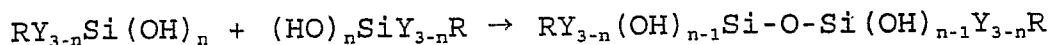
In the context of the present Application, by an "hydrolysable inorganic monomer precursor", we mean any inorganic molecule which is activated by hydrolysis to a polymerisable inorganic monomer, which, on polycondensation with similar hydrolysed or partially hydrolysed monomers, forms inorganic oligomers, and ultimately an inorganic network. The term "inorganic" is used to denote the presence in the precursor molecule of an inorganic element, typically one giving rise to an oxide ceramic material, e.g. silicon, aluminium, titanium, zirconium, yttrium, or other transition metals.

Considering the first step of the process in more detail, the first hydrolysable inorganic monomer precursors, RSiY_3 , may be selected from a variety of materials. However, it is critical that the R-Si bond should not be hydrolysable, as otherwise the organic group R may be lost to the final structure. It is preferred that group R itself is chemically stable, and in particular that it is stable to hydrolysis in the presence of water or moisture. Suitable examples of the group R include hydrogen, and optionally substituted (cyclo)alkyl, aryl, alkenyl, amido, epoxy, (meth)acrylic, styrenic, nitrile, anhydride, ester, phosphino, halide, amino, mercapto and cyanate groups, and mixtures thereof. Preferred R groups

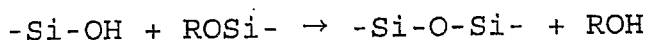
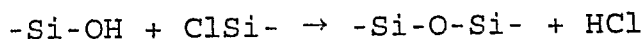
are selected from (cyclo)alkyl, aryl and alkenyl groups, optionally substituted with groups selected from epoxy, vinyl, (meth)acrylic and cyanate groups.

It is further preferred that the size of the R group be selected so that the final composition is liquid in nature, enabling its application as a coating composition.

The Y groups in the first hydrolysable inorganic monomer precursors may be the same as or different to one another, although typically they are the same. The Si-Y bond is a highly reactive bond which readily undergoes hydrolysis to form a silanol group, ie. Si-OH. Suitable examples of Y groups are alkoxy, acetoxy groups, amine and nitrate groups and halogen atoms. Once formed, a silanol group can condense via a water-liberating reaction with another silanol group according to the following reaction sequence:



Alternatively, condensation may proceed in a heterofunctional manner when different hydrolysable inorganic monomer precursors are present, as is discussed in more detail below, such as shown in the following two reaction sequences:



The process of the present invention may involve the use of a single type of hydrolysable inorganic monomer precursor, having the formula RSiY_3 . Alternatively, different hydrolysable inorganic monomer precursors may be used, for instance differing in the nature and/or number of

organic groups R and/or the nature and/or number of the hydrolysable groups Y.

By way of example, first hydrolysable inorganic monomer precursors may be used having different R groups, for instance RSiY_3 , R^1SiY_3 , etc., the R and R^1 groups being selected to provide particular mechanical and/or chemical properties in the final product. In this regard, the present invention is not limited to the use of two different types of first hydrolysable monomer precursors, but may involve the use of more than two different types of the monomer precursors, provided that adequate control over the process is maintained so as to achieve the desired level of incorporation of the different R groups into the final product.

As mentioned above, and in addition or alternatively to the use of first hydrolysable inorganic monomer precursors having different R and/or Y groups, the process may involve the use of hydrolysable inorganic monomer precursors differing in the number of hydrolysable groups Y. In particular, hydrolysable inorganic monomer precursors having the general formula $\text{R}_n\text{SiY}_{4-n}$, in which n is 0, 2 or 3, R is an organic group, for instance selected from those groups given for R above, the R-Si bond is a non-hydrolysable bond, and the R groups are the same as or different to one another, and each Y group is the same as or different to each other Y group and is selected from chemically-reactive groups such that each Si-Y bond is hydrolysable to form a Si-OH bond, and mixtures of such monomer precursors, may be used in addition to the first hydrolysable monomer precursors, RSiY_3 . In the following, these additional monomer precursors are termed "second hydrolysable inorganic monomer precursors".

By way of example, hydrolysable inorganic monomer precursors having four hydrolysable bonds, ie., having the

formula SiY_4 ($n=0$), may be used in addition to the first hydrolysable inorganic monomer precursors.

In addition, or alternatively, the process may involve the use of hydrolysable inorganic monomer precursors having fewer hydrolysable bonds than the first hydrolysable inorganic monomer precursors, for instance having a formula selected from R_2SiY_2 ($n=2$) and R_3SiY ($n=3$), and mixtures thereof.

In the context of any of the second hydrolysable inorganic monomer precursors mentioned above, the nature of the groups R and Y are as defined above for the first organic monomer precursors. For clarity, however, the groups R and/or Y in the second hydrolysable inorganic monomer precursors may be the same as or different to the groups R and/or Y in the first hydrolysable inorganic monomer precursors.

Suitable examples of first hydrolysable inorganic monomer precursors and second hydrolysable inorganic monomer precursors having the formula RSiY_2 or R_3SiY include:

- (i) (alkyl)alkoxysilanes such as trimethoxysilane, triethoxysilane, tri-n-propoxysilane, dimethoxysilane, diethoxysilane, di-iso-propoxysilane, monomethoxysilane, monoethoxysilane, monobutoxysilane, methyldimethoxysilane, ethyldiethoxysilane, dimethylmethoxysilane, di-iso-propylisopropoxysilane, methyltrimethoxysilane, ethyltriethoxysilane, n-propyltri-n-propoxysilane, butyltributoxysilane, dimethyldimethoxysilane, diethyldiethoxysilane, di-iso-propyl-di-iso-propoxysilane, dibutyldibutoxysilane, trimethylmethoxysilane, triethylethoxysilane, tri-n-propyl-n-propoxysilane, tributylbutoxysilane, phenyltrimethoxysilane, diphenyldiethoxysilane and triphenylmethoxysilane;
- (ii) (alkyl)alkoxysilanes having an isocyanato group such as 3-isocyanatopropyltrimethoxysilane, 3-isocyanatopropyltriethoxysilane, 3-isocyanatopropylmethyldimethoxysilane,

3-isocyanatopropylethyldiethoxysilane, 3-isocyanatopropyl-dimethyl-iso-propoxysilane, 3-isocyanatopropyl-diethyl-ethoxysilane, 2-isocyanatoethyl-diethyl-butoxysilane, di(3-isocyanatopropyl)-diethoxysilane, di(3-isocyanatopropyl)-methylethoxysilane, and ethoxytriisocyanatosilane;

(iii) (alkyl)alkoxysilanes having an epoxy group such as 3-glycidoxypropyl-trimethoxysilane, 3-glycidoxypropyl-triethoxysilane, 3-glycidoxypropyl-methyl-dimethoxysilane, 3-glycidoxypropyl-methyl-diethoxysilane, 3-glycidoxypropyl-dimethyl-ethoxysilane, 2-(3,4-epoxycyclohexyl)-ethyl-trimethoxysilane, and 3,4-epoxybutyl-trimethoxysilane;

(iv) (alkyl)alkoxysilanes having a carboxyl group such as carboxymethyl-triethoxysilane and carboxymethyl-diethoxysilane;

(v) alkoxysilanes having an acid anhydride group such as 3-(triethoxysilyl)-2-methylpropylsuccinic anhydride;

(vi) alkoxysilanes having an acid halide group such as 2-(4-chlorosulphonylphenyl)-ethyl-triethoxysilane;

(vii) (alkyl)alkoxysilanes having an amino group such as N-2-(aminoethyl)-3-aminopropyl-triethoxysilane, N-2-(aminoethyl)-3-aminopropyl-methyl-dimethoxysilane, and N-phenyl-3-aminopropyl-trimethoxysilane;

(viii) (alkyl)alkoxysilanes having a thiol group such as 3-mercaptopropyl-trimethoxy-silane, 3-mercaptopropyl-triethoxysilane, 2-mercaptoethyl-triethoxysilane, and 3-mercaptopropyl-methyl-dimethoxysilane;

(ix) (alkyl)alkoxysilanes having a vinyl group such as vinyl-trimethoxysilane, vinyl-triethoxysilane, and vinyl-methyl-diethoxysilane;

(x) (alkyl)alkoxysilanes having an acrylate or methacrylate group such as 3-methacryloxy-propyl-trimethoxysilane, 3-methacryloxypropyl-triethoxysilane, 3-methacryloxypropyl-methyl-dimethyl-silane and 3-acryloxypropyl-triethoxysilane;

(xi) (alkyl)alkoxysilanes having a halogen atom such as triethoxyfluorosilane, 3-chloropropyltrimethoxysilane, 3-bromoalkylalkoxysilane, and 2-chloroethylmethyldimethoxysilane;

(xii) (alkyl)alkoxysilanes having a halogenated alkyl ligand such as (3,3,3-trifluoropropyl)trimethoxysilane and 1H,1H,2H,2H-perfluorodecyltriethoxysilane; and

(xiii) (alkyl)alkoxysilanes employing an alkoxy group as a functional group such as isopropyltri-isopropoxysilane and tri-isopropylisopropoxysilane.

In the above compounds the alkyl group may be replaced by cycloalkyl group, an aryl group or an alkenyl group, and may optionally be substituted preferably with a (meth)acrylate group or an epoxy group. Where hydrolytic stability is desired in the final product, those hydrolysable monomer precursors having hydrolysable R groups should be avoided.

Suitable examples of second hydrolysable inorganic monomer precursors having the formula SiY_4 include silicon tetra-alkoxides, such as tetramethoxysilane, tetramethoxysilane, tetraisopropoxy-silane and tetrabutoxysilane.

The process may also, or alternatively, involve the use of hydrolysable inorganic monomer precursors containing an inorganic atom other than silicon, for instance having the formula MY_n , in which M is typically a metal, n is the valency of the metal, and each Y group is the same or different to one another and is selected from chemically-reactive groups such that each M-Y bond is hydrolysable to a M-OH bond.

Suitable examples of such materials include:

- i) titanium tetra-alkoxides such as titanium tetra-n-propoxide, titanium tetra-iso-propoxide and titanium tetrabutoxide;
- ii) aluminium tetra-alkoxides such as aluminium tri-

secbutoxide, aluminium tri-n-butoxide aluminium tri-isopropoxide;

(iii) zirconium tetra-alkoxides such as zirconium tetra-n-propoxide, zirconium tetra-iso-propoxide and zirconium tetrabutoxide; and

iv) metal alkoxides such as copper dimethoxide, barium diethoxide, boron trimethoxide, gallium triethoxide, germanium tetraethoxide, lead tetrabutoxide, tantalum penta-n-propoxide and tungsten hexaethoxide.

The process may also, or alternatively, involve the use of hydrolysable inorganic monomer precursors of the generic formula $(R_2Si)_xY_2$, in which $x \geq 1$, the R-Si bond is a non-hydrolysable bond and R is defined above (and each R group may be the same as or different to each other R group) and Y is a chemically reactive group with each Si-Y bond being hydrolysable to Si-OH. Suitable examples of the group Y (which may be the same as or different to one another) include chlorine, acetoxy, amine, oxime (ie., $R_2C=NOSi$) and alkoxy. The integer x may vary from 1 to a large number, for instance up to or even greater than 100, giving rise to multi-silicon polymers.

When the process involves the use of hydrolysable inorganic monomer precursors which differ in the number of hydrolysable groups present, it is critical that at least 50 mole%, preferably more than 60 mole%, more preferably at least 70 mole% and most preferably at least 80 mole% or higher, for instance at least 90 mole%, of the total hydrolysable inorganic monomer precursors present should be first hydrolysable inorganic monomer precursors, in order to obtain the most desirable properties for coating applications.

The hydrophilic/hydrophobic character of the R groups(s) will determine the behaviour of the final product when exposed to water. This behaviour can be modified by appropriate selection of solvent. For example, the

tendency towards the repulsion of water of an aliphatic hydrocarbon can be changed by the use of a protic solvent, such as alcohol, compared to an aprotic one, such as tetrahydrofuran.

When the process involves the use of different hydrolysable inorganic monomer precursors it is preferred that hydrolysis of the different hydrolysable inorganic monomer precursors be conducted separately so as to avoid competition for the water molecules present, which may otherwise result in an inhomogeneous or undesirable distribution of monomers, and in particular the organic groups associated therewith, in the final product. After separate partial hydrolysis, the different inorganic oligomers formed are mixed together prior to subjecting to the quenching step that is to follow.

In order to hydrolyse the hydrolysable inorganic monomer precursors, water is either added to the hydrolysable inorganic monomer precursors, or is synthesised *in situ*. Typically, hydrolysis is achieved by formation of an homogeneous mixture with water and, optionally, an organic solvent. Alternatively, the precursors may be dissolved in an organic solvent and water added to the resulting solution in a controlled manner, to avoid the uncontrolled development of agglomerations of partially-hydrolysed molecules. Suitable organic solvents include low boiling point organic liquids, for instance having a boiling point lower than 100°C, such as alcohols.

Preferably, the mixture of water and hydrolysable monomer precursors is mixed to ensure that as many precursor molecules are exposed to water as possible, thereby achieving as homogeneous hydrolysis and condensation as possible.

If, as is less preferred, water is to be synthesised *in situ* in the reaction mixture, this can be achieved, for

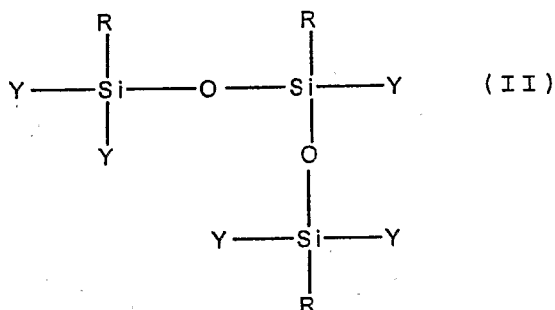
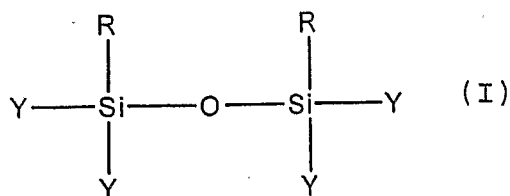
example, by adding an alcohol to the hydrolysable inorganic monomer precursors and then a weak acid, for example acetic acid, again in a controlled manner. In this case, and as described above, it is preferred that separate partial hydrolysis of different hydrolysable inorganic monomer precursors is carried out, followed by mixing together of the different inorganic oligomers formed.

A catalyst may be used to initiate hydrolysis of the hydrolysable inorganic monomer precursors, provided that the catalyst does not react with the inorganic monomer precursors, or affect the nature of the species formed on hydrolysis. Suitable catalysts include mineral acids such as hydrochloric acid, sulphuric acid and nitric acid. Only a small amount of acid is needed for this purpose. Although, depending upon the nature of the inorganic monomer precursors, hydrolysis may proceed spontaneously.

The amount of water used for hydrolysis should generally be sufficient to hydrolyse at least one of the hydrolysable bonds present in each of the inorganic monomer precursor molecules. However, preferably the amount of water, and the conditions of the hydrolysis reaction, are selected so as to achieve hydrolysis of only one or at most two of the hydrolysable bonds present in the first hydrolysable inorganic monomer precursors, as this will dictate the types of structure that are achieved in the second step of the process.

As explained above, part of the first step of the process involves at least partial condensation, but not complete condensation, of the monomers formed on hydrolysis to form inorganic oligomers. The degree of condensation which takes place may be determined by, for example, NMR. Preferably the degree of condensation is such that the majority of oligomers formed from first hydrolysable monomer precursors have one of the following formulae in which each or some of the R groups may be the same or

different:



More preferably a majority of the oligomers have the formula (I), and most preferably most (for instance at least 80 mole% or even at least 90 mole%) of the oligomers have the formula (I).

The first, hydrolysis, step of the process can vary in duration, for instance it may take less than an hour or many days, depending upon the properties required in the final product. Longer durations are believed to result in greater connectivity of the resulting inorganic network, and thus greater molecular weight.

Once sufficient time for some condensation to occur, or for the desired degree of condensation to occur, has lapsed, the mixture is quenched into water to fully hydrolyse the species present and to create conditions that favour complete hydrolysis and further condensation. The detailed nature of the structures created depends upon the nature and concentration of the hydrolysable inorganic monomer precursors used, the solvent, the initial hydrolysing conditions and the co-condensation conditions (time, temperature, pH). In practice, the hydrolysis and

condensation reactions of the first step of the process may be allowed to proceed for a period ranging from a matter of minutes, typically at least 10 minutes, to 24 hours or more.

Quenching can be achieved either by adding water to the liquid composition obtained in the first step of the process, or by adding the liquid composition to water, preferably in a single step. The volume of water used in the quenching step, in combination with any water used in the first step of the process and any water liberated as a result of condensation in that step, should be greater than the stoichiometric amount of water required to achieve total hydrolysis (ie. of all hydrolysable bonds) of all the hydrolysable inorganic monomer precursors. Preferably, the amount of water is at least twice, and more preferably at least five times, this stoichiometric amount. Further condensation is then allowed to proceed, with stirring, typically for a matter of hours up to a number of days, depending upon the properties required in the final product, and whether it is desired that this product should be only partially condensed or essentially completely condensed.

The resulting product is then dried. In the context of this Application "drying" includes the removal of any free water and volatiles, for instance by heating to elevated temperature, typically in the range 40 to 80°C.

The dried product is then ready for use, for instance as a coating composition, or in bulk form, or it may be further modified prior to use. For instance, the product may be cross-linked (or cured) and/or modified to include further organic character to thereby modify the properties of the final product, and/or it may be dehydrated, to reduce or prevent further reaction during use. Solvent may be added to the composition, to improve shelf-life.

Cross-linking, or curing, of the product may be

achieved through the dependent organic R groups, and/or via residual silanols, to form a variety of 3-dimensional structures.

Cross-linking of the organic groups may be achieved by any of the conventional means, for instance by the use of suitable cross-linking reagents or processing conditions, or both, selected to promote intermolecular cross-linking rather than intramolecular cross-linking. For example, epoxy-containing R groups may be cross-linked, or further polymerised, using reagents which act as accelerators or hardeners, for instance amines, or using Lewis acids.

While the dried product might not contain many residual silanols, these can nonetheless influence the behaviour of the product during curing and after curing. Condensation of some or all of these residual silanols may be particularly desirable where further condensation during use of the product would adversely affect the properties of the product. The residual silanols can be made to undergo self-condensation by the use of suitable condensation catalysts, such as triethylamine or tin catalysts, such as tin (II) ethyl hexanoate, or by the selection of suitable reaction conditions known in the art.

Alternatively, condensation of residual silanols may be achieved by the addition of further silanol-containing species or other species condensable with the residual silanols already present in the product. Suitable materials are those having the generic formula $R_nSiY'_{4-n}$, in which n is 0 to 3, R is an organic group as defined above, with each R-Si bond being a non-hydrolysable bond and each R group being the same as or different to each other R group, and Y' is a species that will allow siloxane formation through silanol condensation or other routes, with each Y' group being the same as or different to each other Y' group.

For instance, silanol-containing species for use in said condensation may be prepared by hydrolysis of hydrolysable inorganic monomer precursors having the generic formula $R_nSiY'_{4-n}$, in which each Si-Y' bond is hydrolysable to Si-OH, with Y' being selected, for instance, from those groups given for Y above in the context of first hydrolysable inorganic monomer precursors. Such hydrolysis results in species such as, but not limited to, $R_2Si(OH)_2$ and $R_3Si(OH)$.

Typically, these silanol-containing species will be added to the dried product in the presence of a condensation agent, such as tin (II) ethyl hexanoate, to promote condensation.

Another option mentioned above to effect condensation of the residual silanols is to add other species condensable with those silanols and having the generic formula $R_nSiY'_{4-n}$, in which the Si-Y' bond might not be hydrolysable directly, or at all, to Si-OH. Such species include materials commonly used as derivatising agents to render glass surfaces hydrophobic, and examples of such materials are well known in the art. For instance, materials having the generic formula R_3SiY' are suitable for this purpose, in which R is as defined above and Y' is, for instance, chlorine. For instance, one particular example of such a derivatising agent is trimethylchlorosilane.

Yet another option to effect silanol condensation is to use a material having the generic formula $(R_2Si)_xY_2$, as defined above in the context of the second hydrolysable inorganic monomer precursors, and to hydrolyse this prior to addition to the dried product.

In addition to, or as an alternative to, reducing the residual silanol content by condensation, this may be achieved *via* at least partial dehydration, and preferably substantially complete dehydration. Dehydration is

achieved by any of the conventional methods known in the art. For instance, the dried product may be dissolved in any suitable solvent, for instance tetrahydrofuran (THF), and free water removed via a molecular sieve. Alternatively, dehydration can be further aided by the use of a condensation catalyst, such as triethylamine dissolved in THF and placed over a molecular sieve. After a period of dehydrating the dried product, the volatile solvent is evaporated off to leave a fully or partially dehydrated product.

While, in the above, further condensation of residual silanols has been described as conducted on the dried product, it might be desirable to effect some condensation prior to drying or prior to complete drying of the product. For instance, it might be desirable to effect condensation on a product that has been at least partially dehydrated after drying to remove free water.

Further, while dehydration has been described above as conducted on the dried product, at least partial dehydration may be conducted at earlier stages in the process.

The process of the present invention is capable of giving rise to a wide variety of product structures. The tendency towards a "cage" or "ladder" structure in the final product is controlled by the process parameters, for instance the type and/or concentration of the oligomers formed; the solvent employed; the time and temperature of the mixing step; the concentration during the quenching step; the time and temperature under which quenching is carried out; and the method of recovering the final product.

Should the cross-linked density of the product be less than the theoretical 100%, the product can still be considered to be reactive, which may or may not be acceptable according to the application to which the

material is to be put. If this is unacceptable, various options to achieve further cross-linking, and to reduce reactivity, are described above.

For coating applications, cross-linking through organic (ie. R) groups may be initiated prior to coating, and taken to completion either prior to coating or after coating, on to a substrate, for instance using known irradiation (eg. UV), thermal or chemical methods. If cross-linking is taken to completion prior to coating it may be desirable to dissolve the composition in a solvent in order to coat the composition on to a substrate, and then to evaporate the solvent in order to dry the coated composition.

Before or after any cross-linking, or further condensation, the product obtained on drying (the third step of the process), may be mixed with an organic monomer or oligomer (generally referred to in the following as "polymerisable organic species"), which may then be further polymerised, or an organic polymer, such as a latex.

The nature of the polymerisable organic species is selected according to the properties required in the final product. Typically, the polymerisable organic species will be selected to provide strength and abrasion-resistance and, where desired, transparency. Furthermore, if chemical resistance is required, for instance resistance to swelling or other damage on contact with a solvent, it is desirable to employ polymerisable organic species capable of forming two-dimensional or three-dimensional, i.e. cross-linked, polymer networks. Such polymerisable organic species may be considered as having difunctional or trifunctional reactivity, in that they possess two or more reactive sites available for polymerisation.

For coating applications, preferred polymerisable organic species are those which, upon polymerisation, form thermosetting polymers. Examples of suitable polymerisable

organic species include carbonates, esters such as terephthalates, epoxy-containing materials, methyl (meth)acrylates, urethanes, and other difunctional or trifunctional monomers such as some urethane acrylates, unsaturated aliphatic hydrocarbons, and mixtures thereof. Urethane precursors, such as isocyanates or diisocyanates and polyols, and urethane acrylates are particularly preferred. Organometallic monomers may also be used, but in this case they will not contain hydrolysable bonds.

Preferably, the polymerisable organic species polymerise at relatively low temperature, e.g. lower than 150°C, after addition of a suitable initiator, or by irradiation, e.g. with UV or IR light, or bombardment with X-rays or electron beams, so as to be applicable as coatings for thermoplastic materials or thermosetting materials having low melting points.

Polymerisation of the polymerisable organic species may be initiated in any conventional manner, which will be determined by the nature of the polymerisable organic species. It will normally involve the use of a polymerisation initiator.

For coating applications, substantial organic polymerisation is usually delayed until after coating on to a substrate. Therefore, if heat is used to initiate or accelerate organic polymerisation, the temperature should be selected so as not to have any deleterious effect on the substrate to which the coating is to be applied. In the case of thermoplastic or thermosetting substrates, relatively low temperatures should be used, typically lower than 150°C, and more typically in the range 30 to 80°C. Where a chemical polymerisation initiator is used, this may mean delaying addition of this until just prior to, or possibly during, the coating operation.

The proportion of organic polymer incorporated into the final product depends on the properties required in the

final products.

The properties of the final product may be further adjusted through the use of additives conventional in the art.

When used as a coating composition, the composition may be applied to a substrate by any conventional means, for example dipping, spraying, roll coating or brushing. The composition may be applied to a wide variety of substrates, and is particularly suitable coating polymeric materials having relatively low melting points, for example of 150°C or lower. Examples of such polymeric materials include thermoplastic materials and thermosetting materials such as polycarbonates, polyesters such as polyacrylates and polyterephthalates, polyurethanes, and polyacrylics. The enhanced scratch/abrasion and chemical resistance imparted to these materials by way of the coatings of the present invention allows them to be considerably more widely utilised than they are at present.

The coating composition may also be used to coat substrates selected from glass, metals including soft metals such as aluminium, brass and silver, ceramic materials, and natural materials such as leather and wood, or synthetic substitutes for these materials. It finds particular use as a coating for glass, and glass substitutes. For example, it may be used to coat building or vehicle, windows and windscreens, e.g. for automobile, aircraft and trains; spectacle lenses; camera lenses; protective visors; optical filters and light casings, e.g. headlamp clusters; compact discs; display screens, e.g. in personal computers and mobile phones; and to protect white goods, e.g. refrigerators and washing machines, and brown goods e.g. audiovisual equipment.

The composition of the present invention also finds use as a catalyst coating on a variety of substrates. For this application it is preferred that the composition

should not be cross-linked, so as to maintain its liquid nature.

The composition of the present invention also finds use in bonding together at least two articles. For instance, the composition may be applied to the surface of one or each article, the surfaces to be bonded brought together, and the composition cured to form a secure bond.

The process of the present invention is also capable of producing materials which find use as bulk materials rather than as coatings. In this case, the material may be shaped, for instance by moulding, or otherwise formed into a wide variety of different articles.

The present invention is further illustrated by the following Examples.

Examples

Example 1 - Methacrylate silane resin

A mixture of 111.1g of industrial methylated spirit (IMS), 16.3g of water and 0.16g of 37% HCl were thoroughly stirred and then added to 150.0g 3-trimethoxysilylpropyl methacrylate. This mixture was stirred vigorously for 4 hours, and was then poured (or quenched) into 555g of distilled water. The quenched mixture was stirred vigorously for at least 18 hours before being poured into a large polypropylene container and heated at approximately 50°C for approximately 6 hours to remove the water. The remaining viscous liquid (resin) was then recovered.

Example 2 - Methacrylate silane coating

10.0g of the resin produced in Example 1 was diluted with 30.0g of IMS and 0.1g of the photoinitiator Irgacure 184 was added. After thorough mixing this solution was flow coated onto a Lexan polycarbonate plaque. The coated plaque was dried in an air atmosphere for 5 minutes at 50°C and then cured using UV light.

Example 3 - Methacrylate silane and urethane acrylate coating

9.0g of the resin produced in Example 1 was diluted with 27.0g of industrial methylated spirit and stirred to give an homogeneous solution. To this solution 1.0g of aliphatic urethane acrylate 260GP25 was added and 0.1g of the photoinitiator Irgacure 184. After stirring to achieve an homogeneous solution, the liquid was deposited by flow coating onto a Lexan polycarbonate plaque. The coated plaque was dried in an air atmosphere for 5 minutes at 50°C and then cured using UV light.

Example 4 - Acrylate silane resin

A mixture of 117.8g of industrial methylated spirit (IMS), 17.3g of water and 0.17g of 37% HCl were thoroughly stirred and then added to 150.0g 3-trimethoxysilylpropyl acrylate. This mixture was stirred vigorously for 4 hours, and was then poured (or quenched) into 570g of distilled water. The quenched mixture was stirred vigorously for at least 18 hours before being poured into a large polypropylene container and heated at approximately 50°C for 6 hours to remove the water. The remaining viscous liquid (resin) was then recovered.

Example 5 - Acrylate silane coating

10.0g of the resin produced in Example 4 was diluted with 30.0g of IMS and 0.1g of the photoinitiator Irgacure 184 was added, as was 0.1g of FC4430 (from 3M Corporation) as a flow agent. After thorough mixing this solution was flow coated onto a Lexan polycarbonate plaque. The coated plaque was dried in an air atmosphere for 5 minutes at 50°C and then cured using UV light.

Example 6 - Acrylate silane and urethane acrylate coating

9.0g of the resin produced in Example 4 was diluted with 27.0g of industrial methylated spirit and stirred to give an homogeneous solution. To this solution 1.0g of aliphatic urethane acrylate 260GP25 was added and 0.1g of the photoinitiator Irgacure 184. After stirring to achieve an homogeneous solution, the liquid was deposited by flow

coating onto a Lexan polycarbonate plaque. The coated plaque was dried in an air atmosphere for 5 minutes at 50°C and then cured using UV light.

Example 7 - Epoxy silane resin

A mixture of 77.9g of industrial methylated spirit (IMS) and 11.4g of distilled water were thoroughly stirred and then added to 100.0g of 3-glycidoxypropyltrimethoxysilane. This mixture was stirred vigorously for 4 hours, and was then poured (or quenched) into 379g of distilled water. The quenched mixture was stirred vigorously for at least 18 hours before being poured into a large polypropylene container and heated at approximately 50°C for approximately 6 hours to remove the water. The remaining viscous liquid (resin) was then recovered.

Example 8 - Epoxy silane and diaminoctane coating

5.0g of the resin produced in Example 7 was diluted in 15.0g of IMS and stirred to give an homogeneous liquid. To this liquid was added 1.08g of diaminoctane. The mixture was vigorously stirred for 5 minutes and then deposited as a coating onto a Lexan polycarbonate plaque. The coated plaque was then dried and cured in an air atmosphere at 130°C for 18 hours.

Example 9 - Epoxy silane and xylylenediamine coating

5.0g of the resin produced in Example 7 was diluted in 15.0g of IMS and stirred to give an homogeneous liquid. To this liquid was added 1.02g of xylylenediamine. The mixture was vigorously stirred for 5 minutes and then deposited as a coating onto a Lexan polycarbonate plaque. The coated plaque was then dried and cured in an air atmosphere at 130°C for 18 hours.

Example 10 - Mixed epoxy-phenyl silane resin

Component A and Component B were separately made up.

Component A. 7.0g of 3-glycidoxypropyltrimethoxysilane was placed in a beaker, and an intimate mixture of 5.5g of IMS and 0.80g of water was added thereto.

Component B. 40.0g of phenyltrimethoxysilane was placed in a beaker, and an intimate mixture of 37.1g of IMS and 5.45g of water was added thereto.

Components A and B were stirred, separately, in sealed beakers for about one hour, after which they were combined and stirred for about 4 hours, again in a sealed beaker. This mixture was stirred vigorously for 4 hours, and was then poured (or quenched) into 192g of distilled water. The quenched mixture was stirred vigorously for at least 18 hours before being poured into a large polypropylene container and heated at approximately 50°C for approximately 6 hours to remove the water. The remaining viscous liquid (resin) was then recovered.

Example 11 - Mixed epoxy-phenyl silane diaminoctane coating

5.0g of the resin produced in Example 10 was diluted in 15.0g of IMS and stirred to give an homogeneous liquid. To this liquid was added 0.17g of diaminoctane. The mixture was vigorously stirred for 5 minutes and then deposited as a coating onto a Lexan polycarbonate plaque. The coated plaque was then dried and cured in an air atmosphere at 130°C for 18 hours.

Example 12 - Cyclohexylepoxysilane resin

A mixture of 44.9g of industrial methylated spirit (IMS) and 6.59g of distilled water were thoroughly stirred and then added to 60.0g of 2-(3,4-epoxycyclohexyl)ethyltrimethoxy-silane. This mixture was stirred vigorously for 4 hours, and was then poured (or quenched) into 223g of distilled water. The quenched mixture was stirred vigorously for at least 18 hours before being poured into a large polypropylene container and heated at approximately 50°C for approximately 6 hours to remove the water. The remaining viscous liquid (resin) was then recovered.

Example 13 - Cyclohexylepoxysilane diaminoctane coating

5.0g of the resin produced in Example 12 was diluted in 15.0g of IMS and stirred to give an homogeneous liquid. To this liquid was added 0.20g of diaminoctane. The mixture was vigorously stirred for 5 minutes and then deposited as a coating onto a Lexan polycarbonate plaque. The coated plaque was then dried and cured in an air atmosphere at 130°C for 18 hours.

Example 14 - Aminosilane resin

A mixture of 49.9g of industrial methylated spirit (IMS) and 7.32g of distilled water were thoroughly stirred and then added to 60.0g of 3-aminopropyltriethoxysilane. This mixture was stirred vigorously for 4 hours, and was then poured (or quenched) into 234g of distilled water. The quenched mixture was stirred vigorously for at least 18 hours before being poured into a large polypropylene container and heated at approximately 50°C for approximately 6 hours to remove the water. The remaining viscous liquid (resin) was then recovered.

Example 15 - Mixed epoxy resin

Component A and Component B were separately made up.

Component A. 40.0g of 3-glycidoxypropyltrimethoxysilane was placed in a beaker, and an intimate mixture of 31.1g of IMS and 4.57g of water was added thereto.

Component B. 5.0g of tetraethoxysilane was placed in a beaker, and an intimate mixture of 4.4g of IMS and 0.65g of water was added thereto.

Components A and B were the stirred, separately, in sealed beakers for about one hour, after which they were combined and stirred for about 4 hours, again in a sealed beaker. This mixture was stirred vigorously for 4 hours, and was then poured (or quenched) into 172g of distilled water. The quenched mixture was stirred vigorously for at least 18 hours before being poured into a large polypropylene container and heated at approximately 50°C for approximately 6 hours to remove the water. The

remaining viscous liquid (resin) was then recovered.

Example 16 - Dehydration of Resin

1.5 g of the resin produced in Example 4 was dissolved in a mixture of 0.25g triethylamine and 4.5g of THF. The solution was then placed over dried 4A type molecular sieve. After 24 hours, the solvent was evaporated off and the dehydrated resin was dissolved in 4.5g IMS and 0.1g of photoinitiator Irgacure 184 was added. After thorough mixing, the solution was then deposited by flow coating onto a Lexan polycarbonate plaque. The coated plaque was air dried for five minutes and then cured using UV light.

Example 17 - Capping of Residual Silanols

1.5 g of the resin produced in Example 4 was dissolved in a mixture of 0.25g triethylamine, 4.5g of THF and 0.25g of chlorotrimethylsilane. After 24 hours, the mixture was filtered through a 1µm filter to remove the solid chloride salt. The solvent was evaporated off and the resin was dissolved in 4.5g IMS and 0.1g of photoinitiator Irgacure 184 was added. After thorough mixing the solution was then deposited by flow coating onto a Lexan polycarbonate plaque. The coated plaque was air dried for five minutes and then cured using UV light.

Example 18 - Capping of Residual Silanols with R_2SiY_2 Type Silane

1.5 g of the resin produced in Example 4 was dissolved in a mixture of 0.25g triethylamine, 4.5g of THF and 0.5g of diethoxydimethylsilane. The solution was then placed over dried 4A type molecular sieve. After 24 hours, the solvent was evaporated off and the resin was dissolved in 4.5g IMS and 0.1g of photoinitiator Irgacure 184 was added. After thorough mixing the solution was then deposited by flow coating onto a Lexan polycarbonate plaque. The coated plaque was air dried for five minutes and then cured using UV light.

Example 19 - Capping of Residual Silanols with Long Chain

Silanes

1.5 g of the resin produced in Example 4 was dissolved in a mixture of 0.25g triethylamine, 4.5g of THF and 2g of hydroxy-terminated polydimethylsiloxane (viscosity = 90-150 centi-stokes). The solution was then placed over dried 4A type molecular sieve. After 24 hours, the solvent was evaporated off and the resin was dissolved in 4.5g IMS and 0.1g of photoinitiator Irgacure 184 was added. After thorough mixing the solution was then deposited by flow coating onto a Lexan polycarbonate plaque. The coated plaque was air dried for five minutes and then cured using UV light.

Example 20 - Incorporation of R_2SiY_2 Silane into Sol

A mixture of 117.8g of industrial methylated spirit (IMS), 17.3 grams of water and 0.17g of 37%HCl were thoroughly stirred and then added to 150.0g of 3-trimethoxysilylpropyl acrylate. This mixture was stirred for 240 minutes. Separately a mixture of 58.3g of industrial methylated spirit (IMS), 5.46 grams of water and 0.1g of 37%HCl were thoroughly stirred and then added to 45.0g of diethoxydimethylsilane and mixed for five minutes. The two silane solutions were then mixed and stirred together for two hours, and was then poured (or quenched) into 570g of distilled water. The quenched mixture was stirred vigorously for at least 18 hours before being poured into a large polypropylene container and heated at approximately 50°C for six hours to remove the water. The remaining liquid resin was then recovered.

Example 21 - Dehydration of Resin - Use as Adhesive/Sealant

1.5 g of the resin produced in Example 4 was dissolved in a mixture of 0.25g triethylamine and 4.5g of THF. The solution was then placed over dried 4A type molecular sieve. After 24 hours, the solvent was evaporated off and the dehydrated resin was dissolved in 0.5g IMS and 0.1g of photoinitiator Irgacure 184 was added together with 0.5g of

urethane acrylate 260Gp25. After thorough mixing the solution was then syringed onto a polyester sheet. A second sheet was placed over the first and the two were pressed together to give a bond line of ~50 μ m. The sandwich structure was then cured under a UV light for five minutes and the resin mixture gave an adhesive seal.

CLAIMS

1. A process for forming a composition comprising organosilsesquioxanes, the process comprising the following steps:

(1) partially hydrolysing hydrolysable inorganic monomer precursors comprising at least 50 mole% of first hydrolysable inorganic monomer precursors having the formula RSiY_3 , in which R is an organic group, the R-Si bond is a non-hydrolysable bond, each Y group is the same as or different to each other Y group and is selected from chemically-reactive groups such that each Si-Y bond is hydrolysable to form a Si-OH bond, to form inorganic monomers and allowing partial condensation of the inorganic monomers to form a liquid composition comprising inorganic oligomers;

(2) prior to complete condensation of the inorganic monomers, quenching the liquid composition with an amount of water which, in combination with the water used in step (1) and any water liberated by condensation of the inorganic monomers in step (1), is in excess of the stoichiometric amount of water required to achieve complete hydrolysis of all the hydrolysable inorganic monomer precursors present; and

(3) drying the composition.

2. A process according to claim 1, wherein the hydrolysable inorganic monomer precursors comprise more than 60 mole %, preferably at least 70 mole %, and more preferably at least 80 mole %, of first hydrolysable inorganic monomer precursors.

3. A process according to claim 1 or claim 2, wherein the R group in the first hydrolysable inorganic monomer precursors is stable to hydrolysis.

4. A process according to claim 1 or claim 2, wherein the R group in the first hydrolysable inorganic monomer precursors is selected from hydrogen and (cyclo)alkyl, aryl, alkenyl, amido, epoxy, (meth)acrylic, styrenic, nitrile, anhydride, ester, phosphino, halide, amino, mercapto and cyanate groups, and mixtures thereof.

5. A process according to any preceding claim, wherein the Y groups in the first hydrolysable monomer precursors are selected from alkoxy, acetoxy and nitrate groups, and halogen atoms, and are preferably alkoxy groups.

6. A process according to any preceding claim, wherein when step (1) comprises partially hydrolysing different hydrolysable inorganic monomer precursors said different hydrolysable inorganic monomer precursors are hydrolysed separately from one another, followed by partial condensation of the resulting different inorganic monomers, and then mixing of the resulting liquid compositions prior to carrying out step (2).

7. A process according to any preceding claim, wherein the first hydrolysable monomer precursors comprise molecules having different R groups, wherein preferably in step (1) the different first hydrolysable monomer precursors are hydrolysed separately from one another, and allowed to partially condense, and the resulting liquid compositions are then mixed together prior to carrying out step (2).

8. A process according to any preceding claim, wherein the hydrolysable inorganic monomer precursors additionally comprise second hydrolysable monomer precursors having the formula R_nSiY_{4-n} , in which n is 0, 2 or 3, each R-Si bond is

a non-hydrolysable bond, R is an organic group and each R group is the same as or different to each other R group, and each Y group is the same as or different to each other Y group and is selected from chemically-reactive groups such that each Si-Y bond is hydrolysable to Si-OH, and wherein preferably in step (1) the first and second hydrolysable monomer precursors are partially hydrolysed separately from one another, and allowed to partially condense, and the resulting liquid compositions are then mixed together prior to carrying out step (2).

9. A process according to claim 8, wherein the second hydrolysable inorganic monomer precursors have the formula SiY_4 .

10. A process according to any preceding claim, wherein the hydrolysable inorganic monomer precursors additionally comprise hydrolysable monomer precursors having the formula MY_n , in which M is a metal, n is the valency of the metal, and each Y group is the same as or different to each other Y group and is selected from chemically-reactive groups such that each M-Y bond is hydrolysable to a M-OH bond, and wherein preferably in step (1) the different hydrolysable monomer precursors are partially hydrolysed separately from one another, and allowed to partially condense, and the resulting liquid compositions are then mixed together prior to carrying out step (2).

11. A process according to any preceding claim, wherein the hydrolysable inorganic monomer precursors additionally comprise hydrolysable monomer precursors having the formula $(\text{R}_2\text{Si})_x\text{Y}_2$, in which $x \geq 1$, each R-Si bond is a non-hydrolysable bond, R is an organic group and each R group is the same as or different to each other R group, and each Y group is the same as or different to each other Y group

and is selected from chemically-reactive groups such that each Si-Y bond is hydrolysable to Si-OH, and wherein preferably in step (1) the different hydrolysable monomer precursors are partially hydrolysed separately from one another, and allowed to partially condense, and the resulting liquid compositions are then mixed together prior to carrying out step (2).

12. A process according to any preceding claim, wherein in step (1) at least 80 mole%, preferably at least 90 mole%, of the first hydrolysable monomer precursors undergo hydrolysis and condensation via one of the Si-Y bonds to form inorganic oligomers having the formula $\text{RY}_2\text{-Si-O-SiY}_2\text{R}$.

13. A process according to any preceding claim, wherein the amount of water used in step (2), in combination with the amount of water used in the hydrolysis of step (1) and any water liberated by condensation in step (1), is at least twice, and preferably at least 5 times, the stoichiometric amount of water required for complete hydrolysis of all the hydrolysable monomer precursors present.

14. A process according to any preceding claim, which comprises, as step (4), dehydrating the composition obtained in step (3) to obtain a dehydrated composition.

15. A process according to any preceding claim, which further comprises cross-linking the composition obtained in step (3) via residual silanols present in the composition to obtain a cross-linked composition.

16. A process according to any of claims 1 to 13, which further comprises mixing the composition obtained in step (3) with organic monomers or oligomers.

17. A process according to claim 14, which further comprises mixing the dehydrated composition obtained in step (4) with organic monomers or oligomers.
18. A process according to claim 15, which further comprises mixing the cross-linked composition obtained with organic monomers or oligomers.
19. A process according to any of claims 16 to 18, which further comprises polymerising the organic monomers or oligomers.
20. A process according to any of claims 1 to 13, which comprises mixing the composition obtained in step (3) with a liquid organic polymer.
21. A process according to claim 14, which further comprises mixing the dehydrated composition obtained in step (4) with a liquid organic polymer.
22. A process according to claim 15, which further comprises mixing the cross-linked composition obtained with a liquid organic polymer.
23. A process according to any of claims 1 to 13, which further comprises cross-linking the composition obtained in step (3) via the R groups to obtain a cross-linked composition.
24. A process according to claim 14, which further comprises cross-linking the composition obtained in step (4) via the R groups to obtain a cross-linked composition.
25. A composition comprising organosilsesquioxanes which

is obtainable by a process defined in any preceding claim.

26. A process for providing a coating on a substrate comprising applying to the substrate a composition obtainable by a process defined in any of claims 1 to 24, and optionally cross-linking the composition.

27. A process for providing a coating on a substrate comprising applying to the substrate a composition obtainable by a process defined in any of claims 1 to 18, polymerising the organic monomers or oligomers, and optionally cross-linking the composition.

28. A process according to claim 26 or claim 27, wherein the substrate is selected from thermoplastic polymeric substrates, eg. polycarbonate and acrylic resins.

29. A process according to claim 26 or claim 27, wherein the substrate is selected from metals, including soft metals such as aluminium, brass and silver.

30. A process for forming an article comprising shaping a composition as defined in claim 25.

31. A process for bonding together at least two articles comprising applying to the surface of one or each article a composition as defined in a obtainable by a process as defined in any of claims 1 to 24, bringing the surfaces into contact with one another, and then cross-linking the composition to form a bond.

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2006/003750

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	C08G77/06	C08G77/14
	C08L83/04	C09D183/04
		C09J183/04
		C08G77/20
		C08G77/26
		C08G77/58
		C09D183/06
		C09J183/06
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 C09D C09J		
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, CHEM ABS Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 217 082 A (GEN ELECTRIC [US]) 23 December 1970 (1970-12-23) page 2, lines 39-96 page 6, lines 46-52	1-5,7, 13,25
Y	claims; example 1	8-10
A	US 2003/212228 A1 (DAI JIE [SG] ET AL) 13 November 2003 (2003-11-13) paragraph [0017]; example 1	1-24, 26-31 25
X		
A	JP 2005 122815 A (FUJI PHOTO FILM CO LTD) 12 May 2005 (2005-05-12) abstract	1,23,24, 26,27
Y	paragraphs [0111] - [0118], [0123]	8,9
A	US 6 586 104 B2 (MATSUDA MASAYUKI [JP] ET AL) 1 July 2003 (2003-07-01)	1
Y	claims; example 1	10
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<input checked="" type="checkbox"/>	Further documents are listed in the continuation of Box C.	<input checked="" type="checkbox"/>
		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	*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	
E earlier document but published on or after the international filing date	*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	
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)	*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.	
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P document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search	Date of mailing of the international search report	
28 February 2007	07/03/2007	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Hein, Friedrich	

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2006/003750

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	BE 538 417 A (RHONE-POULENC) 3 July 1959 (1959-07-03) résumé -----	1-14
A	FR 1 469 072 A (GEN ELECTRIC) 28 April 1967 (1967-04-28) résumé -----	1,12
A	JP 2004 284221 A (SUMITOMO CHEMICAL CO) 14 October 2004 (2004-10-14) abstract paragraphs [0048] - [0056] -----	1-31
A	US 2003/191269 A1 (KO MIN-JIN [KR] ET AL) 9 October 2003 (2003-10-09) example 1 -----	1
A	US 2003/224286 A1 (BARCLAY GEORGE G [US] ET AL BARCLAY GEORGE G [US] ET AL) 4 December 2003 (2003-12-04) example 1 -----	1,14
A	EP 0 410 564 A2 (DOW CORNING [US]) 30 January 1991 (1991-01-30) claims -----	25

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2006/003750

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 1217082	A	23-12-1970	DE 1668172 A1 FR 1562918 A US 3450672 A	13-05-1971 11-04-1969 17-06-1969
US 2003212228	A1	13-11-2003	CN 1454919 A SG 102047 A1	12-11-2003 27-02-2004
JP 2005122815	A	12-05-2005	NONE	
US 6586104	B2	01-07-2003	WO 9749775 A1 TW 442544 B US 2002011182 A1	31-12-1997 23-06-2001 31-01-2002
BE 538417	A		NONE	
FR 1469072	A	28-04-1967	NONE	
JP 2004284221	A	14-10-2004	NONE	
US 2003191269	A1	09-10-2003	AT 343608 T CN 1458947 A EP 1328571 A1 JP 2004509191 T WO 0222710 A1 KR 20020021864 A	15-11-2006 26-11-2003 23-07-2003 25-03-2004 21-03-2002 23-03-2002
US 2003224286	A1	04-12-2003	NONE	
EP 0410564	A2	30-01-1991	CA 2018609 A1 DE 69023566 D1 DE 69023566 T2 ES 2081932 T3 JP 2059220 C JP 3066730 A JP 7094556 B US 4999397 A	28-01-1991 21-12-1995 30-05-1996 16-03-1996 10-06-1996 22-03-1991 11-10-1995 12-03-1991