HIGH BOILING INHIBITORS FOR DISTILLABLE, POLYMERIZABLE MONOMERS

Abstract: Disclosed herein are compounds of structure (I), wherein $R_1$, $R_2$, and $R_3$ are organic radicals of C$_1$ to C$_{30}$, such that the combination of the three contains at least twelve carbon atoms and $R_3$ is bound to the methylene carbon atom between X and the aromatic ring by at least one saturated carbon atom, allowing it to be easily separated from the polymerizable monomer by distillation; $R_1$ and $R_2$ having sufficient steric bulk to protect the phenol from reacting with an alkoxy group or halogen bound to silicon; and X is a neutral heterocyclic radical of oxygen, nitrogen, or phosphorus; and their use as inhibitors for the polymerization of (meth)acryloylsilanes.
HIGH BOILING INHIBITORS FOR DISTILLABLE, POLYMERIZABLE MONOMERS

BACKGROUND OF THE INVENTION

1. Field of Invention

The present invention relates to polymerization inhibitors for use in the stabilization of polymerizable monomers, compositions containing them, and their preparation. More particularly, this invention is directed to the use of these inhibitors as stabilizers during the production and subsequent storage of acryloxysilanes and methacryloxysilanes.

2. Description of Related Art

Acryloxysilanes and methacryloxysilanes are chemically reactive materials that are useful in many commercial applications. For example, such compounds are useful as coupling agents to bond organic compounds to inorganic materials. In particular, 3-methacryloxypropyltrimethoxysilane is widely used as a coupling agent in enhancing the performance of fiberglass-reinforced products.

U.S. Patent No. 3,258,477 discloses silanes characterized by a trifunctional silicon atom at one end of the molecule and an acryloxy group on the other end of the molecule and to aqueous solutions formed therefrom.

U. S. Patent No. 3,305,483 discloses a method of preparation and compositions of a variety of hindered phenolic benzylamines, which are antioxidants, wherein the linkage between benzylic nitrogen and aromatic rings is limited to a methylene group.

U. S. Patent No. 4,709,067 discloses a process for preparing, purifying and/or storing methacryloxy or acryloxy containing organosilicon compounds without the undesirable polymerization normally associated with the methacrylate bonds. In an alternative
embodiment, the process includes the addition of certain stabilizers, and in particular diketone or ketoester stabilizers.

U.S. Patent No. 4,780,555 discloses a method for preparing acryl-functional halosilanes by reacting a halosilane with an acryloxy or methacryloxy-functional organic compound in the presence of a platinum hydrosilation catalyst and a stabilizing amount of phenothiazine, wherein the reaction mixture is contacted with an oxygen-containing inert gas. A method for stabilizing the above reaction mixture by contacting it with the oxygen-containing gas is also disclosed.

U.S. Patent No. 5,103,032 discloses compositions containing an acryloxisilane or a methacryloxisilane and an N,N-dialkylaminomethylene phenol in an amount at least sufficient to inhibit polymerization of the silane during its formation, purification, and storage. Methods for producing such compositions are also provided.

U.S. Patent No. 5,145,979 discloses processes for the preparation of \( \gamma \)-methacryloxypropylsilane compounds which comprise carrying out the reaction of allyl methacrylate with a hydrosilane compound in the presence of a platinum catalyst, while allowing at least one of a hindered phenol compound and an aromatic amine compound to coexist in the reaction system with an alkylamine compound or an amide compound, or with a gas containing molecular oxygen, or with a phenol compound having an aminoalkylene group. By using these processes as provided, gelation of the reaction mixture in the reaction system and during the course of purification thereof by distillation is said to be effectively avoided and the desired \( \gamma \)-methacryloxypropylsilane compounds obtained in good yield.
U.S. Patent No. 5,616,753 discloses a method for inhibiting the polymerization of unsaturated silanes by the addition of a non-aromatic stable free radical during any of the steps of the formation of the desired silane, the purification of the desired silane, and to the desired silanes, as well as compositions of the inhibitors and the silanes. Particular classes of silanes to be inhibited include acryloxy-, methacryloxy-, and vinyl- functional silanes. The free radicals for use as inhibitors include various nitroxides. The free radicals are effective as inhibitors at elevated temperatures, for extended periods of time, and even in the absence of molecular oxygen.

U.S. Patent No. 5,616,774 and commonly assigned E. P. No. 744,392 disclose hindered phenolic benzylamines wherein the methylene linkages between benzylic nitrogen and aromatic rings are substituted with aromatic or otherwise multiply bonded carbon groups or heteroatom groups, wherein said amines are isolated or non-isolated intermediates leading to the ultimate preparation of stable hindered quinone methides.

U.S. Patent No. 5,723,643 discloses a method to make high-purity acryloxy- or methacryloxy-functional organosilicon compounds in high yields by inhibiting gelation of the reaction product during preparation. The method comprises (A) reacting an acrylate or methacrylate ester of an alcohol comprising an aliphatically unsaturated bond or a phenol comprising an aliphatically unsaturated bond with a (B) SiH-functional silicon compound in the presence of (C) a hydrosilylation reaction catalyst and (D) a polymerization inhibitor described by a given formula. The method can further comprise distillation of the reaction mixture resulting from the reaction of component (A) and (B) in the presence of component (D).
U.S. Patent No. 5,914,418 discloses a method for inhibiting polymerization of acrylic-functional silanes comprising forming a mixture comprising an acrylic-functional silane and a polymerization inhibitor described by a given formula.

The disclosures of the foregoing are incorporated herein by reference in their entirety.

SUMMARY OF THE INVENTION

This invention relates to the composition and method of preparation of polymerization inhibitors and compositions containing them for use in the stabilization of polymerizable monomers. Furthermore, this invention encompasses the use of these inhibitors as stabilizers during the production and storage of acryloxy silanes and methacryloxy silanes. (For convenience, the term "(meth)acryloxy silanes" will be used hereinafter to refer to both acryloxy silanes and methacryloxy silanes.) The inhibitors described herein and potential degradation products thereof can be easily removed from the (meth)acryloxy silane monomers by distillation, thus allowing for them to be easily substituted by a second polymerization inhibitor with more desirable physical properties.

More specifically, the present invention is directed to a compound of the structure

```
R_1
OH

R_2

R_3
```

wherein
R₁, R₂, and R₃ are organic radicals of C₁ to C₂₀, such that the combination of the three contain at least twelve carbon atoms and R₃ is bound to the methylene carbon atom between X and the aromatic ring by at least one saturated carbon atom, allowing it to be easily separated from the polymerizable monomer by distillation;

R₁ and R₂ have sufficient steric bulk to protect the phenol from reacting with an alkoxy group or halogen bound to silicon; and

X is a neutral heteroatomic radical of oxygen, nitrogen, or phosphorus.

In another aspect, the present invention is directed to a composition comprising a (meth)acryloxysilane and a stabilizing amount of at least one compound of the structure

![Chemical structure](image)

wherein

R₁, R₂, and R₃ are organic radicals of C₁ to C₂₀, such that the combination of the three contain at least twelve carbon atoms and R₃ is bound to the methylene carbon atom between X and the aromatic ring by at least one saturated carbon atom, allowing it to be easily separated from the polymerizable monomer by distillation;

R₁ and R₂ have sufficient steric bulk to protect the phenol from reacting with an alkoxy group or halogen bound to silicon; and

X is a neutral heteroatomic radical of oxygen, nitrogen, or phosphorus.
In still another aspect, the present invention is directed to a method for the stabilization of (meth)acryloxysilanes during their production, storage, or both comprising adding thereto a compound of the structure

\[
\begin{align*}
\text{R}_1 & \quad \text{OH} \\
\text{R}_2 & \\
\text{X} & \\
\text{R}_3 & 
\end{align*}
\]

wherein

\( \text{R}_1, \text{R}_2, \text{and} \text{R}_3 \) are organic radicals of \( \text{C}_1 \) to \( \text{C}_{20} \), such that the combination of the three contain at least twelve carbon atoms and \( \text{R}_3 \) is bound to the methylene carbon atom between \( \text{X} \) and the aromatic ring by at least one saturated carbon atom, allowing it to be easily separated from the polymerizable monomer by distillation; \( \text{R}_1 \) and \( \text{R}_2 \) have sufficient steric bulk to protect the phenol from reacting with an alkoxy group or halogen bound to silicon; and \( \text{X} \) is a neutral heteroatomic radical of oxygen, nitrogen, or phosphorus.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

(Meth)acryloxysilanes can be prepared by the known reaction between organosilicon compounds having an Si-H function group and acryloxy and methacryloxy compounds having additional aliphatic unsaturation, as has been described, for example, by Plueddemann and Clark in U.S. Patent No. 3,258,477 and by Chu and Kanner in U.S. Patent No. 4,709,067. For example, 3-methacryloxypropyltrimethoxysilane (MAOP-TMS) can be prepared by the
known reaction of allyl methacrylate with trimethoxysilane, as shown in the following equation (1):

\[
\begin{align*}
\text{CH}_2=\text{C(\text{CH}_3)C(O)OCH}_2\text{CH}=\text{CH}_2 + (\text{CH}_3\text{O})_3\text{Si-H} \longrightarrow \\
\text{CH}_2=\text{C(\text{CH}_3)C(O)OCH}_2\text{CH}_2\text{CH}_2\text{-Si(OCH}_3)_3
\end{align*}
\]

MAOP-TMS

Likewise, reaction of allyl methacrylate with trichlorosilane, \(\text{Cl}_3\text{Si-H}\), provides 3-methacryloxypropyltrichlorosilane, which, in turn, can be reacted with methanol to produce MAOP-TMS. When allyl acrylate is used in place of allyl methacrylate, the corresponding acryloxypropyltrimethoxy- (or trichloro-) silanes are provided. Owing to the exothermic nature of such hydrosilation reactions and the presence of catalytic platinum-hydrosilane complexes, polymerization of the highly reactive acryloxy silane and methacryloxy silane product can occur as product is formed. Such polymerization can also be induced during esterification of the trichlorosilane intermediate to the corresponding trialkoxysilane product, such as, for example, during reaction of the aforementioned 3-methacryloxypropyltrichlorosilane with methanol to produce MAOP-TMS.

Undesirable polymerization can also occur during purification of the crude reaction product. Typically, purification is accomplished by distillation, which is preferably carried out at as low a temperature as is feasible to minimize polymerization. Even purified product may tend to polymerize during storage prior to end use. Depending on the extent of such polymerization during initial formation, purification, and storage of acryloxy- and methacryloxy silanes, thickening, and even gelling, may occur, resulting in increased maintenance to remove the thickened or gelled material from equipment or in unsalable product.
In U.S. Patent No. 5,103,032, Turner et al. describe the use of N,N-dialkylaminomethylene phenols as polymerization inhibitors for acryloxy- and methacryloxy silanes during their formation, purification, and storage. Similarly, in U.S. Patent No. 5,145,979, Takatsuna et al. describe the use of similar compounds for the same purpose.

It has been found that, during the course of the hydrosilation reaction, this inhibitor gradually breaks down to form 2,6-di-t-butylresor (also referred to as BHT or Ionol). In the case of the commercially important MAOP-TMS, this butylated cresol is known to co-distill with the product. This hurts the end use of this material in certain applications by imparting an undesirable water insolubility characteristic to the final product.

**Inhibitor Composition**

The inhibitors of the present invention are substituted phenols of the formula

\[
\begin{align*}
\text{OH} & \quad R_1 \\
& \quad \quad \quad R_2 \\
& \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad
\end{align*}
\]

wherein R₁, R₂, and R₃ are organic radicals of C₁ to C₂₀, such that the combination of the three impart sufficient mass to the molecule to allow it and its potential degradation products to be easily separated from the polymerizable monomer by distillation. The potential degradation products are XH, with X as defined above, and the substituted phenol above wherein X is
replaced by hydrogen. The volatilities, i.e., boiling points of XH and the phenolic degradation product are preferably selected such that XH has a boiling point below the silane product, and the phenolic degradation product has a boiling point above the silane product. Alternatively, both potential degradation products can be selected with boiling points above that of the silane product. The difference in boiling point, above or below that of the silane product, is preferably at least 20° C at the desired distillation pressure. For MAOP-TMS, this is preferably accomplished when R₁, R₂, and R₃ total at least twelve carbon atoms and R₃ is bound to the methylene carbon atom between X and the aromatic ring by at least one saturated carbon atom. X is a neutral heteroatomic radical of oxygen, nitrogen, or phosphorus and is selected from a broad range of oxygen, nitrogen, and phosphorus-bound radicals, including esters, ethers, amines, imines, phosphines, phosphates, and the like, with amines, carbon esters, silyl ethers, and phosphines being preferred. The morpholino group is a particularly preferred embodiment of X. Furthermore, R₁ and R₂ should have sufficient steric bulk so as to protect the phenol from reacting with an alkoxy group or halogen bound to silicon, for example, t-butyl, iso-octyl, t-amyl, t-hexyl, s-butyl, s-amyl, and the like.

Specific examples of such compounds include:

2,6-di-tert-butyl-4-(1-dimethylamino-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-morpholino-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-trimethylsilyloxy-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-triphenylsilyloxy-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-diphenylmethylsilyloxy-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-tri-iso-propylsilyloxy-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-diphenylphospho-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-benzoyl-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-dimethylaminotridecyl)phenol,
2,6-di-tert-butyl-4-(1-morpholinotridecyl)phenol,
2,6-di-tert-butyl-4-(1-trimethylsilyloxytridecyl)phenol,

2,6-di-tert-butyl-4-(1-diphenylphosphotridecyl)phenol,
2,6-di-tert-butyl-4-(1-benzoyltridecyl)phenol,
2,6-di-t-butyl-4-(1-benzoylpentyl)phenol,
2,6-di-t-butyl-4-(morpholinopentyl)phenol,
2,6-di-t-butyl-4-(1-dimethylaminopentyl)phenol, and

2,6-di-isooctyl-4-(1-dimethylamino-3-phenylpropyl)phenol.

**Inhibitor Synthesis**

The inhibitors described above can be made by the use of standard organic reactions. For example, the Grignard reaction between phenethylmagnesium chloride and 3,5-di-t-butyl-4-hydroxybenzaldehyde produces 2,6-di-t-butyl-4-(1-hydroxy-3-phenylpropyl)phenol. This alcohol can be silylated by known techniques with the corresponding chlorosilane to yield the "silyloxy" derivatives listed above. Further treatment of the trimethylsilyloxy derivative with an amine, such as morpholine or dimethylamine, produces the amine derivatives described.

Treatment of the product alcohol from the Grignard reaction with chlorophosphines yields the phosphinite derivatives. Similarly, the organic esters can be made by reacting the same alcohol with the corresponding acid chloride or anhydride. Many synthetic variations will lead to the desired inhibitors.
The present invention also encompasses the use of such inhibitors and inhibitor-containing compositions in the production of (meth)acryloxysilanes. It further encompasses the separation of the inhibitor from the (meth)acryloxysilane and its substitution by a second polymerization inhibitor having more desirable physical properties, such as water solubility.

In the (meth)acryloxysilanes that are stabilized with the above described phenolic inhibitors, the (meth)acryloxy moieties are bonded to silicon through an alkylene or alkyleneoxy bridge and the silicon is further bonded to alkoxy groups or halides. Preferably, the silanes are those encompassed by the general formula A shown below:

General Formula A:

\[ \text{CH}_2=\text{C}((\text{R'})\text{CO}_2-(\text{R''}),(\text{R''}),(\text{R'})_b\text{Si}_3 \]

wherein:

R is hydrogen or methyl;
R' is alkylene of two to four carbon atoms;
R'' is alkylene, preferably of from one to four carbon atoms;
Y is halide, alkoxy, or alkoxy-substituted alkoxy groups, wherein the alkoxy preferably has from one to four carbon atoms, or an alkyl group, preferably of from one to four carbon atoms;
a is zero to ten, preferably zero to five;
b is at least one; and

a+b is a number from one to eleven, preferably one to six.
The \( R' \) and \( R'' \) groups can be linear or branched, and any combination of such groups can be present. The divalent \( R' \) group is exemplified by ethylene (-CH\(_2\)CH\(_2\)-) and higher homologous groups, such as propylene, isopropylene, butylene, and the like. \( R'' \) can be any such alkylene groups and, in addition, can be methylene.

The Si-bonded \( Y \) groups are preferably any \( C_1-C_4 \) linear or branched alkoxy groups (e.g., methoxy, ethoxy, isopropoxy, and the like) or \( C_1-C_4 \) alkoxy-substituted \( C_1-C_4 \) alkoxy groups (e.g., \( \beta \)-methoxyethoxy), or halides, such as, in particular, chlorine and bromine.

Illustrative of such (meth)acryloxysilanes that can be stabilized as described herein are:

- 3-acryloxypropyltrimethoxysilane
- 3-acryloxypropylmethyldimethoxysilane
- 3-acryloxypropylmethyldimethoxysilane
- 3-methacryloxypropyltrimethoxysilane
- 3-methacryloxyisobutyltrimethoxysilane
- 3-methacryloxyisobutylmethyldimethoxysilane
- 3-methacryloxypropylmethyldimethoxysilane
- 3-methacryloxypropyldimethylethoxysilane
- 3-methacryloxypropyldimethylethoxysilane
- 3-methacryloxypropyldimethylethoxysilane
- 3-methacryloxypropyltriethoxysilane
- 3-methacryloxypropyltrichlorosilane
- 3-methacryloxypropyltrimethylsilane
- 3-methacryloxyisobutyltrichlorosilane
- 3-methacryloxypropyltrischlorosilane
- 3-methacryloxypropyltrischlorosilane
- 3-methacryloxypropyltrischlorosilane
- 3-methacryloxypropyl[tris(beta-methoxyethoxy)]silane

The above-described (meth)acryloxysilanes are prepared by methods known in the art, such as those described in the aforementioned U.S. Patent Nos. 3,258,477 and 4,709,067, which are incorporated herein by reference. For example, (meth)acryloxysilanes encompassed by general formula A above can be prepared by the reaction of an SiH functional compound.
and an ester of acrylic or methacrylic acid wherein the ester moiety has an ethylenically unsaturated group, as shown by the following equation (1):

\[
\begin{align*}
\text{CH}_2=C(R')\text{CO}_2(R'\text{O})_2-(\text{CH}_2)_c-C(\text{R''})=\text{CH}_2 + Y_3\text{Si-H} & \rightarrow \\
\text{CH}_2=C(R')\text{CO}_2(R'\text{O})_2-(\text{CH}_2)_c-\text{CH}(\text{R''})-\text{CH}_2-\text{SiY}_3
\end{align*}
\]

where: \( R, R', a, \) and \( Y \) are as defined above with respect to general formula \( A; R'' \) is hydrogen or methyl; and \( c \) is zero or one; and the \( -(\text{CH}_2)_c-\text{CH}(\text{R''})\text{CH}_2- \) group is illustrative of the \( R'' \) alkylene group of general formula \( A. \) The hydrosilation reactions encompassed by equation (1) are normally effected at a temperature from about 70° C to about 120° C in the presence of a platinum-containing catalyst, such as those described in U.S. Patent No. 4,709,067. The platinum-containing hydrosilation catalyst may be chosen from the group of supported platinum-catalysts, such as platinum on \( \gamma \)-alumina or on charcoal, or from the group of homogeneous soluble platinum complexes, such as chloroplatinic acid bis-(ethylene platinous)chloride, dichlorobis(acetonitrile)platinum (II), cis-dichlorobis(triphenylphosphine)platinum (II), tetrakis(triphenylphosphine)platinum (O) or other soluble platinum complexes well known in the art. The soluble platinum complexes are normally in solution in solvents such as isopropanol, acetonitrile, or 1,2-dimethoxyethane.

The concentration of the platinum catalyst required depends on reaction temperature and time, but is generally used in the range of from about 2 to about 100 ppm and preferably from about 10 to about 25 ppm, based on the total weight of the hydrosilane and allyl methacrylate.

With reference to the hydrosilation reaction of equation (1), it is to be understood that when the desired product is a (meth)acryloxytrialkoxyssilane (i.e., when \( Y \) of general formula \( A \) is an alkoxy group), the \( Y \) group of the \( H\text{-SiY}_3 \) reactant of equation (1) can be halogen, preferably chlorine, or alkoxy. When \( Y \) of the reactant is chlorine, for example, the product of
equation (1) is the corresponding trichlorosilane, which can then be esterified with an alcohol, such as methanol, by methods known in the art to provide the desired trialkoxysilane.

Alternatively, the desired trialkoxysilane can be produced directly by the hydrosilation reaction of equation (1) by the use of a trialkoxysilane reactant, H-SiY₃, in which Y is alkoxy. Y may also be an alkyl group, preferably of from one to four carbon atoms, more preferably a methyl group, such that the corresponding silanes with two, one, or even no hydrolyzable groups are encompassed by the present invention. It is to be understood, therefore, that the inhibitors used in the present invention can be provided to the reaction mixture that produces the desired product directly, or to an intermediate reaction mixture.

In addition to hydrosilation, the (meth)acryloxysilanes that are stabilized as described herein can be prepared by the reaction of a tertiary amine or alkali metal salt of acrylic or methacrylic acid with a chloroalkylsilane as described in U.S. Patent Nos. 3,258,477 and 4,946,977. This chloroalkylsilane is of the formula:

\[
\text{CICH}_2\text{CH}_2\text{Si}(R^1)_3
\]

wherein \( R^1 \) is an alkoxy or acyloxy radical and \( x \) is 0, 1, 2, or 3. Triethylamine is a preferred amine to form the reactant salt, and the salt as such does not necessarily have to be isolated. Thus, the amine, or alkali metal base, and the chosen acid can simply be mixed, and the chloroalkylsilane added to the mixture in approximately stoichiometric quantities. The reaction is preferably carried out in the presence of an inert organic solvent, such as benzene, toluene, xylene, or cyclohexane, at reaction temperatures of about 100° C to about 150° C.

In accordance with one embodiment of the process of the present invention, the inhibitor is provided to the reaction mixture used to produce the (meth)acryloxysilane to be stabilized. Such (meth)acryloxysilane-forming reaction mixtures include those containing the
above-described hydrosilation reactants (e.g., an ethylenically unsaturated ester of acrylic or methacrylic acid and an SiH functional compound, such as a trialkoxysilane or trihalosilane), as well as mixtures containing a tertiary amine salt or an alkali metal salt of acrylic or methacrylic acid and a chlorosilane (e.g., chloromethyltrimethoxysilane and chloropropyltrimethoxysilane).

In accordance with another embodiment of the present invention, the inhibitor is provided to the (meth)acryloxy silane-containing mixture to be purified by distillation.

The inhibitor may be provided by adding it as a separate stream directly to the zone in which the (meth)acryloxy silane is either to be formed initially or purified. Alternatively, the inhibitor can be provided to the zone as a component of one or more reactant streams, or as a component of the mixture to be distilled. The inhibitor can also be provided to the recovered or final product, such as prior to packaging, storage, or shipping. Preferably, it is added just prior to the process steps requiring inhibition, more preferably using multiple additions of the inhibitor during the overall manufacturing process (initial reaction, purification, and recovery of product). It is to be understood that the inhibitor can be provided at any step of a batch or continuous process for (meth)acryloxy silane manufacture, without departing from the scope of this invention.

The stabilization of (meth)acryloxy silanes is effected by employing the inhibitor in an amount at least sufficient to prohibit polymerization. The particular minimal amount used depends largely on the severity of the conditions to which the silane will be subjected during its initial formation, purification, and storage. For example, in general, the higher the temperature the more susceptible the silane will be to polymerization. Further, the lower the free oxygen content to which the silane or silane-containing medium is exposed, the greater
the tendency of the silane to polymerize. Some oxygen in the vapor space above the
(meth)acryloxysilane is beneficial in inhibiting polymerization; however, as the concentration
of oxygen in the vapor space increases, the level of dissolved oxygen in the silane-containing
medium also increases. High levels of dissolved oxygen within the (meth)acryloxysilane-
containing medium can lead to peroxide formation, which, in turn, can initiate polymerization.
Thus, subjecting the silane or silane-containing medium to high temperatures, and/or to
oxygen levels that promote peroxide formation, substantially increases the minimum effective
amount of inhibitor.

In addition to oxygen level and temperature, other conditions that can induce
polymerization of (meth)acryloxysilanes are metal contaminants, ultraviolet light, and free
radical initiators. Illustrative of the latter are oxygen-derived peroxy and peroxide, as well as
alkoxy, aryloxy, alkyl, and aryl free radicals.

Generally, oxygen levels of approximately 0.1 to 4 percent by volume in nitrogen are
believed to be beneficial in aiding inhibitors in inhibiting polymerization; see U.S. Patent
Number 4,780,555. However, with increasing levels of dissolved oxygen, peroxide radicals
can form to an extent sufficient to initiate polymerization, as noted above, despite the presence
of inhibitors. In order to minimize free radical formation, oxygen levels should not exceed
4 percent by volume of the vapor space throughout the (meth)acryloxysilane-forming reaction
and purification process.

Generally, about 5 to 2,000 ppm (parts by weight per million parts by weight of silane)
of the inhibitor are sufficient to prevent polymerization of (meth)acryloxysilanes. Normally,
no more than about 100 to 500 ppm are required. It is to be understood, however, that
exposure of the (meth)acryloxysilanes to severe conditions will require correspondingly higher
levels of inhibitor, such as about 1,000 ppm or more. For example, high temperature
distillation (160°C to 190°C) or exposure to a combination of conditions that accelerate
polymerization, such as exposure to atmospheric conditions (21 percent oxygen by volume)
and heat (e.g., 140°C) will result in gelling of (meth)acryloxysilanes unless substantially higher
inhibitor levels are used, such as about 1,000 to 2,500 ppm of inhibitor being present during
the (meth)acryloxysilane-forming reaction, with an additional 10 to about 325 ppm of inhibitor
provided during distillation. A final addition of inhibitor can be added to the product in order
to stabilize it during storage and distribution, the preferred range for this purpose being from
about 5 to about 25 ppm.

Included in the scope of the present invention is the use of the phenolic inhibitors
described in combination with other polymerization inhibitors, including those containing
phenolic (-OH), amino (-NH), quinone (O=C), and nitrooxide (N-O) functionality. Illustrative
of such other inhibitors are: hydroquinone; benzoquinone; the monomethyl ether of
hydroquinone (MEHQ); N,N'-diphenyl-p-phenylenediamine; phenothiazine; Iono™;
Isonox™ 129; Ethanol™ 702; Ethanol™ 703; Ethanol™ 330; 2,2,6,6-tetramethyl-1-
piperidinyloxy free radical (TEMPO); 4-hydroxy TEMPO; and mixtures of the foregoing. The
phenolic inhibitor of this invention is present in such combinations in an amount sufficient to
provide a polymerization inhibitor system having improved performance relative to said other
inhibitors or mixtures of said other inhibitors not containing the phenolic inhibitors of this
invention.

The inhibitor is typically provided to the (meth)acryloxysilane-forming reaction and
purification process as a solution. This technique provides more uniform dispersion of the
inhibitor throughout the medium to be stabilized. Any solvent for the phenolic inhibitors of
this invention may be used provided it does not adversely affect product quality or process control. Typically, the solvents selected are aromatic hydrocarbons well known in the art, such as toluene, benzene, xylene and the like, with toluene being preferred.

While the phenolic inhibitors of the present invention are surprisingly good at inhibiting the (meth)acryloxy silane polymerization during the hydrosilylation reaction, when used in higher concentrations they can be detrimental to the physical properties of the product. High concentrations of hindered phenolic inhibitors have a detrimental effect on, for example, the water solubility characteristics of the product. It is in accordance with this invention that these inhibitors can be easily separated from the (meth)acryloxy silane by distillation. This provides an opportunity to replace the phenolic inhibitor with a different inhibitor or combination of inhibitors that may impart more desirable properties to the final (meth)acryloxy silane than the phenolic inhibitor. Such inhibitors may include MEHQ or any of the nitroxyl based inhibitors such as TEMPO or 4-hydroxy-TEMPO described by Turner et al. in U.S. Patent No. 5,616,753, which patent is incorporated herein by reference. In particular, the broader class of polymerizable silanes disclosed by Turner et al. can be inhibited by the inhibitors of the present invention.

Because the phenolic inhibitors described in this invention are typically higher boiling than the (meth)acryloxy silane, the second inhibitor needs to be added prior to or during the distillation to protect the lower boiling methacrylates which come overhead during the distillation. These lower boiling methacrylates, which must be removed, are unreacted allyl methacrylate and isomers thereof from the hydrosilation reaction. There are a number of ways to achieve this outcome known in the art. For example, the lower boiling inhibitor can be added to the (meth)acryloxy silane prior to distillation. In this case, the boiling point of the
lower boiling inhibitor must be such that it co-distills with the methacrylate so that it protects it during all phases of the distillation. Alternatively, the lower boiling inhibitor can be continuously added to the (meth)acryloxy silane feed, to the base of the column or to other feed points in the column. An inhibitor that boils higher than the methacrylate could be added to the top of the distillation column so that it runs counter current to the methacrylate flow. In this last case, however, it may be required that a polymerization inhibitor also be placed into the vessel to which the stripped methacrylate is to be collected. It can also be envisioned that the lower boiling inhibitor can be injected anywhere along the distillation train to protect different segments from polymerization.

The advantages and the important features of the present invention will be more apparent from the following examples. All parts and percentages are by weight unless otherwise specified.

EXAMPLES

Example 1

The procedure used to determine gel time in the examples is as follows:

A thermocouple is used to measure the temperature of the (meth)acryloxy silane sample to be tested. The sample to be tested and a clean Teflon-covered magnetic stir bar are placed in a clean, dry 5 mL vial and sealed. The sample is purged with nitrogen at a rate of 200 cc per minute for 30 minutes to remove oxygen. A thermocouple is placed into the sample and the sample is heated to 140°C in a constant temperature bath. When polymerization begins to occur the viscosity of the sample rises and a temperature gradient is observed. Eventually, with increasing polymerization, the temperature of the (meth)acryloxy silane sample will register as a temperature differential compared to the constant temperature bath. For
purposes of the examples, a sample is considered to have gelled when the temperature within the sample deviates by approximately 2° C from the constant temperature bath and stirring stops.

The results of this test for various compounds are listed in Table 1. Entries 1 to 4 are listed for comparison with some lower boiling analogs. Entry 4 was prepared by silylation of the corresponding alcohol with trimethylchlorosilane. These are comparative examples, which are outside the scope of the present invention. The entries 5 to 11 are examples of the inhibitors with higher boiling points as described herein.

**TABLE 1**

<table>
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<tr>
<th>Entry No.</th>
<th>Compound</th>
<th>140° C Stability (hours)</th>
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<tr>
<td>1</td>
<td>2,6-di-t-butyl-4-methylphenol (BHT)</td>
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<td>2</td>
<td>2,6-di-t-butyl-4-dimethylaminomethylphenol (Ethanol 703)</td>
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<td>3</td>
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<td>15</td>
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<tr>
<td>11</td>
<td>2,6-di-t-butyl-4-(1-dimethylaminotridecyl)phenol</td>
<td>26</td>
</tr>
</tbody>
</table>
Example 2

This example demonstrates the use of these inhibitors under reaction conditions and their separation from the final reaction product by distillation.

(A) Inhibitor use in the synthesis of 3-methacryloxypropyltrimethoxysilane:

To a two-liter round-bottom flask fitted with a mechanical stirrer, reflux condenser, thermometer, and a 3 percent O₂/N₂ sparge set for approximately 100 mL of gas per minute was fed a solution comprising 555.3 grams (4.41 moles) of allyl methacrylate (AMA), 1.05 grams (0.003 mole, 1891 ppm based on the weight of AMA) of 2,6-di-t-butyl-4-(1-morpholino-3-phenylpropyl)phenol, and 19 ppm platinum as chloroplatinic acid based on the weight of the AMA. This solution was added at approximately 4.9 mL/min for 10 minutes. During this time the pot contents were heated to 90° C. After 10 minutes, a second feed of trimethoxysilane (TMS) was started at a feed rate of approximately 4.3 mL/min. The two solutions were fed at these rates for two hours while maintaining a reaction temperature of 90° C. After two hours of feeding the solutions, the pot contents were held at 90° C for an additional two hours. After this time the reaction was cooled. Gas chromatographic analysis of the crude mixture showed that the contents comprised 69.8 percent by weight of the desired product, 3-methacryloxypropyltrimethoxysilane, and 14.7 percent by weight of unreacted AMA and related isomers.

(B) Distillation of the crude 3-methacryloxypropyltrimethoxysilane with replacement of the 2,6-di-t-butyl-4-(1-morpholino-3-phenylpropyl)phenol with 4-methoxyphenol (MEHQ).
To a one-liter three-neck round-bottom flask were charged 458 grams of the crude 3-methacryloyloxypropyltrimethoxysilane made in part (A) of this example and two grams of 4-methoxyphenol (MEHQ). The flask was fitted with an addition funnel, thermometer, and a 10-tray adiabatic Oldershaw column on top of which was fitted a vacuum distillation head. The addition funnel was charged with a solution of two grams of 4-methoxyphenol dissolved in 20 grams of a high molecular weight polyalkylene glycol polyether. This solution was slowly added to the distillation pot throughout the distillation. After the low boiling components were removed three product cuts were taken. The product cuts were taken with temperatures in the distillation head between 95° and 98° C and pressure of 0.5 to 1.0 mm Hg. A total of 306.4 grams of product was collected having an average purity of 97.8 percent. None of the 2,6-di-t-butyl-4-(1-morpholino-3-phenylpropyl)phenol was found in any of the product cuts. A 10 weight percent aliquot of this distilled product in water produced a clear aqueous solution.

Example 3

Synthesis of 2,6-di-t-butyl-4-(1-morpholino-3-phenylpropyl)phenol. This example describes the synthesis of one of the inhibitors described. All of the inhibitors described can be made by this procedure by appropriately substituting either the Grignard reagent, the chlorosilane, or the amine.

(A) 2,6-di-t-butyl-4-(1-hydroxy-3-phenylpropyl)phenol

To a 5-liter, 4-neck round-bottom flask fitted with a mechanical stirrer, reflux condenser, thermometer, and addition funnel were charged 238.5 grams (1.02 moles) of 3,5-di-t-butyl-4-hydroxybenzaldehyde and 979 grams of toluene. To this suspension, a one molar solution of phenethylmagnesium chloride in THF was slowly added such that the pot
temperature slowly rose to 40°C. After the addition of several hundred milliliters of Grignard reagent solution a green sticky solid formed. The addition was halted, an additional 859 mL of toluene was added, and the solution was warmed to 80°C. The remaining Grignard reagent was slowly added while maintaining the pot temperature between 50°C and 70°C.

After the addition was complete, the reaction mixture was stirred at 70°C for one hour. During this time, the green solids dissolved and the reaction mixture formed two liquid phases. After this time, the reaction was cooled and then quenched by slowly adding 80 mL of deionized water. The quenched reaction mixture was then poured into six liters of water. The organic phase was separated and the solvent removed in vacuo. The resulting crude product was then dissolved in warm hexane and filtered. The filtrate was washed with hexane (2 × 100 mL). The hexane portions were combined and solvent removed producing 242 grams (69.8 percent) of a viscous amber oil.

(B) 2,6-di-t-butyl-4-(1-trimethylsilyloxy-3-phenylpropyl)phenol

To a nitrogen-purged 250 mL three-neck round-bottom flask were added 141 grams (0.41 mole) of the 2,6-di-t-butyl-4-(1-hydroxy-3-phenylpropyl)phenol produced in step (A) of this example, 100 mL of toluene, and 54.3 grams (0.50 mole) of trimethylchlorosilane. The addition of the chlorosilane produced a several degree exotherm. The mixture was allowed to stir overnight at ambient temperature. After this time, the reaction mixture was washed with water (3 × 200 mL), dried with sodium sulfate, and filtered. Removal of the hexane gave 148.9 grams of desired product (87.1 percent).

(C) 2,6-di-t-butyl-4-(1-morpholino-3-phenylpropyl)phenol
To a nitrogen-purged, 250 mL, three-neck, round-bottom flask were added the 148.9 grams of the 2,6-di-t-butyl-4-(1-trimethylsilyloxy-3-phenylpropyl)phenol produced in step (B) of this example, 67 grams of hexane, and 45.8 grams (0.53 mole) of morpholine. The mixture was stirred overnight at ambient temperature. After this time, the solvent was removed and the solids recrystallized from a solution of 5 percent toluene in hexane to give pure 2,6-di-t-butyl-4-(1-morpholino-3-phenylpropyl)phenol as a white crystalline solid.

In view of the many changes and modifications that can be made without departing from principles underlying the invention, reference should be made to the appended claims for an understanding of the scope of the protection to be afforded the invention.
CLAIMS

What is claimed is:

1. A compound of the structure

\[
\begin{align*}
\text{R}_1 & \quad \text{OH} \\
\text{X} & \quad \text{R}_3 \\
\text{R}_2
\end{align*}
\]

wherein

9. \( \text{R}_1, \text{R}_2, \) and \( \text{R}_3 \) are organic radicals of \( \text{C}_1 \) to \( \text{C}_{26} \) such that the combination of the three contain at least twelve carbon atoms and \( \text{R}_3 \) is bound to the methylene carbon atom between \( \text{X} \) and the aromatic ring by at least one saturated carbon atom, allowing it to be easily separated from the polymerizable monomer by distillation;

13. \( \text{R}_1 \) and \( \text{R}_2 \) have sufficient steric bulk to protect the phenol from reacting with an alkoxy group or halogen bound to silicon; and

15. \( \text{X} \) is a neutral heteroatomic radical of oxygen, nitrogen, or phosphorus.

2. The compound of claim 1 wherein said compound is selected from the group consisting of:

3. 2,6-di-tert-butyl-4-(1-dimethylamino-3-phenylpropyl)phenol,

4. 2,6-di-tert-butyl-4-(1-morpholino-3-phenylpropyl)phenol,

5. 2,6-di-tert-butyl-4-(1-trimethylsilyloxy-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-triphenylsilyloxy-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-diphenylmethysilyloxy-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-tri-iso-propylsilyloxy-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-diphenylphospho-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-benzoyl-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-dimethylaminotridecyl)phenol,
2,6-di-tert-butyl-4-(1-morpholinotridecyl)phenol,
2,6-di-tert-butyl-4-(1-trimethylsilyloxytridecyl)phenol,
2,6-di-tert-butyl-4-(1-diphenylphosphotridecyl)phenol,
2,6-di-tert-butyl-4-(1-benzoyltridecyl)phenol,
2,6-di-t-butyl-4-(1-benzoylpentyl)phenol,
2,6-di-t-butyl-4-(morpholinopentyl)phenol,
2,6-di-t-butyl-4-(1-dimethylaminopentyl)phenol, and
2,6-di-isoctyl-4-(1-dimethylamino-3-phenylpropyl)phenol.

3. A composition comprising a (meth)acryloxysilane and a stabilizing amount of at least one compound of the structure

\[
\begin{align*}
R_1 & & R_2 \\
\text{OH} & & \\
\text{X} & & R_3
\end{align*}
\]
wherein

R₁, R₂, and R₃ are organic radicals of C₄ to C₂₀, such that the combination of the three contain at least twelve carbon atoms and R₃ is bound to the methylene carbon atom between X and the aromatic ring by at least one saturated carbon atom, allowing it to be easily separated from the polymerizable monomer by distillation;

R₁ and R₂ have sufficient steric bulk to protect the phenol from reacting with an alkoxy group or halogen bound to silicon; and

X is a neutral heteroatomic radical of oxygen, nitrogen, or phosphorus.

4. The composition of claim 3 wherein the compound is selected from the group consisting of:

2,6-di-tert-butyl-4-(1-dimethylamino-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-morpholino-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-trimethylsilyloxy-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-triphenylsilyloxy-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-diphenylmethyloxy-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-tri-iso-propylsilyloxy-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-diphenylphospho-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-benzoyl-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-dimethylaminotridecyl)phenol,
2,6-di-tert-butyl-4-(1-morpholinotridecyl)phenol,
2,6-di-tert-butyl-4-(1-trimethylsilyloxytridecyl)phenol,
2,6-di-tert-butyl-4-(1-diphenylphosphotridecyl)phenol,
15 2,6-di-tert-butyl-4-(1-benzoyltridecyl)phenol,
16 2,6-di-t-butyl-4-(1-benzyloypentyl)phenol,
17 2,6-di-t-butyl-4-(morpholinopentyl)phenol,
18 2,6-di-t-butyl-4-(1-dimethylaminopentyl)phenol, and
19 2,6-di-isooctyl-4-(1-dimethylamino-3-phenylpropyl)phenol.

5. The composition of claim 3 further comprising at least one additional inhibitor selected
   from the group consisting of inhibitors containing phenolic, amino, quinone, or nitroxide
   functionality.

6. The composition of claim 3 wherein the (meth)acryloxysilane is of the structural
   formula
   \[ \text{CH}_2=\text{C}(\text{R})-\text{CO}_2-(\text{R}'\text{O})_a(\text{R}''\text{H})_b-\text{SiY}_3 \]
   wherein:
   5 R is hydrogen or methyl;
   6 R' is alkyne of two to four carbon atoms;
   7 R'' is alkylene;
   8 Y is halide, alkoxy, alkoxy-substituted alkoxy or alkyl;
   9 a is zero to ten;
   10 b is at least one; and
   11 a+b is a number from one to eleven.
7. The composition of claim 6 wherein the (meth)acryloxyisilane is selected from the group consisting of 3-acryloxypropyltrimethoxysilane, 3-acryloxypropyltriethoxysilane, 3-acryloxypropylmethylidimethoxysilane, 3-acryloxypropylmethyldiethoxysilane, 3-acryloxypropyldimethylmethoxysilane, 3-acryloxypropyl(dimethylethoxy) silane, 3-methacryloxypropyltrimethoxysilane, 3-methacryloxyisobutyltrimethoxysilane, 3-methacryloxypropylmethylidimethoxysilane, 3-methacryloxypropylmethyldiethoxysilane, 3-methacryloxypropyl(dimethylethoxy)silane, 3-methacryloxyisobutylmethylidimethoxysilane, 3-methacryloxypropyltriethoxysilane, 3-acryloxypropyltrichlorosilane, 3-methacryloxypropyltrichlorosilane, and 3-methacryloxypropyl[tris(betamethoxyethoxy)]silane.

8. The composition of claim 7 wherein the (meth)acryloxyisilane is 3-methacryloxypropyltrimethoxysilane.
9. A method for the stabilization of (meth)acryloxysilanes during their production, storage, or both comprising adding thereto a compound of the structure

\[
\begin{align*}
&\text{OH} \\
&R_1 - \text{phenyl} - R_2 \\
&X - R_3
\end{align*}
\]

wherein

R₁, R₂, and R₃ are organic radicals of C₁ to C₂₀, such that the combination of the three contain at least twelve carbon atoms and R₃ is bound to the methylene carbon atom between X and the aromatic ring by at least one saturated carbon atom, allowing it to be easily separated from the polymerizable monomer by distillation;

R₁ and R₂ have sufficient steric bulk to protect the phenol from reacting with an alkoxy group or halogen bound to silicon; and

X is a neutral heteroatomic radical of oxygen, nitrogen, or phosphorus.

10. The method of claim 9 wherein the compound is selected from the group consisting of:

2,6-di-tert-butyl-4-(1-dimethylamino-3-phenylpropyl)phenol,

2,6-di-tert-butyl-4-(1-morpholino-3-phenylpropyl)phenol,

2,6-di-tert-butyl-4-(1-trimethylsilyloxy-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-triphenylsilyloxy-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-diphenylmethylsilyloxy-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-tri-isopropylsilyloxy-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-diphenylphospho-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-benzoyl-3-phenylpropyl)phenol,
2,6-di-tert-butyl-4-(1-dimethylaminotridecyl)phenol,
2,6-di-tert-butyl-4-(1-morpholinotridecyl)phenol,
2,6-di-tert-butyl-4-(1-trimethylsilyloxytridecyl)phenol,
2,6-di-tert-butyl-4-(1-diphenylphosphotridecyl)phenol,
2,6-di-tert-butyl-4-(1-benzoyltridecyl)phenol,
2,6-di-t-butyl-4-(1-benzoylpentyl)phenol,
2,6-di-t-butyl-4-(morpholinopentyl)phenol,
2,6-di-t-butyl-4-(1-dimethylaminopentyl)phenol, and
2,6-di-isooctyl-4-(1-dimethylamino-3-phenylpropyl)phenol.

11. The method of claim 9 further comprising the step of adding at least one additional inhibitor selected from the group consisting of inhibitors containing phenolic, amino, quinone, or nitroxide functionality.
12. The method of claim 9 wherein the (meth)acryloxysilane is of the structural formula
   \[ CH_2=\text{C(R)}-\text{CO}_2-(\text{R'}\text{O})_a(\text{R''})_b \text{-SiY}_3 \]
   wherein:
   4 R is hydrogen or methyl;
   5 R' is alkyne of two to four carbon atoms;
   6 R'' is alkyne;
   7 Y is halide, alkoxy, alkoxy-substituted alkoxy or alkyl;
   8 a is zero to ten;
   9 b is at least one; and
   10 a+b is a number from one to eleven.

13. The method of claim 12 wherein the (meth)acryloxysilane is selected from the group
   consisting of 3-acryloxypropyltrimethoxysilane, 3-acryloxypropyltriethoxysilane,
   3-acryloxypropylmethyldimethoxysilane, 3-acryloxypropylmethyldiethoxysilane,
   3-acryloxypropylidimethoxysilane, 3-acryloxypropylidimethylethoxysilane,
   3-methacryloxypropyltrimethoxysilane,
   3-methacryloxyisobutyltrimethoxysilane, 3-methacryloxypropylmethyldimethoxysilane,
   3-methacryloxypropylmethyldiethoxysilane, 3-methacryloxypropylidimethylethoxysilane,
   3-methacryloxypropylidimethylethoxysilane, 3-methacryloxyisobutylmethyldimethoxysilane,
   3-methacryloxypropyltriethoxysilane, 3-acryloxypropyltrichlorosilane,
   3-methacryloxypropyltrimethylsilane, 3-methacryloxypropyltrichlorosilane,
   3-methacryloxyisobutyltrichlorosilane, and 3-methacryloxypropyl[tris(beta-
   methoxyethoxy)]silane.
14. The method of claim 13 wherein the (meth)acryloxy silane is 3-methacryloxypropyltrimethoxysilane.
# INTERNATIONAL SEARCH REPORT

## A. CLASSIFICATION OF SUBJECT MATTER

**IPC 7** C07F7/08 C07F7/18 C07F7/20

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)

**IPC 7** C07F

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

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

BEILSTEIN Data, EPO-Internal, WPI Data, PAJ, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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<td>DATABASE CROSSFIRE BEILSTEIN 'Online!' Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; Database accession no. 2028752 XP002217358 &amp; KUDINOVA ET AL.: BULL ACAD. SCI. USSR. DIV. CHEM. SCI., vol. 27, 1978, page 1313</td>
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<tr>
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<td>Further documents are listed in the continuation of box C.</td>
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<td>Patent family members are listed in annex.</td>
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*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)
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*"E" document member of the same patent family

## Date of the actual completion of the international search

15 November 2002

## Date of mailing of the international search report

26/11/2002

## Name and mailing address of the ISA

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## Authorized officer

Koessler, J-L

Form PCT/ISA/210 (second sheet) (July 1992)
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<td>DATABASE CROSSFIRE BEILSTEIN 'Online! Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; Database accession no. 5386709 XP002217359 abstract &amp; MAEURER ET AL.: CHEM. BER., vol. 125, no. 4, 1992, pages 857-866, ---</td>
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**INTERNATIONAL SEARCH REPORT**

**Box I  Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.☐ Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2.☒ Claims Nos.: 1, 2 (in part)
   because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
   see FURTHER INFORMATION sheet PCT/ISA/210

3.☐ Claims Nos.:
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II  Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1.☐ As all required additional search fees were timely paid by the applicant, this international Search Report covers all searchable claims.

2.☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3.☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4.☐ No required additional search fees were timely paid by the applicant. Consequently, this international Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.
Continuation of Box I.2

Claims Nos.: 1, 2 (in part)

The initial phase of the search revealed a very large number of documents relevant to the issue of novelty. So many documents were retrieved that it is impossible to determine which parts of claim 1 may be said to define subject-matter for which protection might legitimately be sought (Article 6 PCT). For these reasons, a meaningful search over the whole breadth of claim 1 is impossible. Consequently, the search has been restricted to: compounds of claim 1 wherein R1 and R2 is a t-Butyl group and R3 is a radical having at least 4 carbon atoms.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.
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