(54) Title: METHOD OF FORMING AN ENCAPSULANT LAYER FOR A PHOTOVOLTAIC CELL MODULE

(57) Abstract: A method of forming an encapsulant layer for a photovoltaic cell module including a photovoltaic cell layer and an outer layer spaced from the photovoltaic cell layer comprises disposing a silicone composition having a kinematic viscosity of from greater than 0 to less than about 1,000 centistoke (cSt) at 25 °C between the photovoltaic cell layer and the outer layer. The method further comprises polymerizing the silicone composition in situ between the photovoltaic cell layer and the outer layer, thereby forming the encapsulant layer in the photovoltaic cell module.
Declarations under Rule 4.17:
— of inventorship (Rule 4.17(iv))
METHOD OF FORMING AN ENCAPSULANT LAYER FOR A PHOTOVOLTAIC CELL MODULE

BACKGROUND OF THE INVENTION

[0001] This invention generally relates to an encapsulant layer for a photovoltaic cell module and, more specifically, to a method of forming an encapsulant layer for a photovoltaic cell module in situ.

[0002] Photovoltaic cell modules are well known in the art and are available in various sizes and shapes contingent on the desired output and particular climate in which the photovoltaic cell modules are utilized. For example, photovoltaic cell modules may be cylindrical or rectangular. Cylindrical photovoltaic cell modules generally include an outer cylinder and an inner cylinder disposed in the outer cylinder. In particular, the inner cylinder is a photovoltaic layer and the outer cylinder is an outer layer, and an encapsulant layer is disposed therebetween. Viscous silicone gels are not utilized as encapsulant layers in cylindrical photovoltaic cell modules because such viscous silicone gels cannot be poured or otherwise disposed between the inner and outer cylinder without the introduction of trapped air, which has a deleterious effect on output and efficiency of photovoltaic cell modules. Additionally, pressures required to introduce such viscous silicone gels can break or otherwise damage the photovoltaic cell layer and/or the outer layer. Accordingly, silicone fluids are typically utilized to form the encapsulant layer of cylindrical photovoltaic cell modules. However, silicone fluids often include substantial amounts of expensive monomeric silicon compounds, e.g. hexamethyldisiloxane, to lower the viscosity of the silicone fluid such that it can be easily poured. Moreover, if the cylindrical photovoltaic cell is damaged, the silicone fluid flows, i.e., leaks, from the cylindrical photovoltaic cell module, which greatly reduces the output and efficiency of the cylindrical photovoltaic cell module.

SUMMARY OF THE INVENTION

[0003] This invention provides a method of forming an encapsulant layer for a photovoltaic cell module which comprises a photovoltaic cell layer and an outer layer spaced form the photovoltaic cell layer. The method comprises disposing a silicone composition having a kinematic viscosity at 25 °C of from > 0 to less than about 1,000 centistoke (cSt) between the photovoltaic cell layer and the outer layer. The
method further comprises polymerizing the silicone composition in situ between the photovoltaic cell layer and the outer layer, thereby forming the encapsulant layer in the photovoltaic cell module.

BRIEF DESCRIPTION OF THE DRAWINGS

[0004] Other advantages and aspects of this invention may be described in the following detailed description when considered in connection with the accompanying drawings wherein:

[0005] Figure 1 is a schematic top view of a photovoltaic cell module including an encapsulant layer between a photovoltaic cell layer and an outer layer spaced from the photovoltaic cell layer; and

[0006] Figure 2 is a schematic perspective view of the photovoltaic cell module including the encapsulant layer between the photovoltaic cell layer and the outer layer spaced from the photovoltaic cell layer.

DETAILED DESCRIPTION OF THE INVENTION

[0007] Referring to the Figures, wherein like numerals indicate corresponding parts throughout the several views, a photovoltaic cell module 10 is generally shown. This invention provides a method of forming an encapsulant layer 12 for the photovoltaic cell module 10. The invention method is particularly suitable for forming an encapsulant layer 12 for a cylindrical photovoltaic cell module. Alternatively, the invention method may be utilized in photovoltaic cell modules other than cylindrical photovoltaic cell modules, or in applications other than photovoltaic cell modules.

[0008] The method comprises disposing a silicone composition between a photovoltaic cell layer 14 of a photovoltaic cell module 10 and an outer layer 16 spaced from the photovoltaic cell layer 14. The step of disposing the silicone composition between the photovoltaic cell layer 14 and the outer layer 16 typically comprises pouring the silicone composition between photovoltaic cell layer 14 and the outer layer 16. Specifically, the silicone composition has a kinematic viscosity at 25 °C such that the silicone composition is flowable, or pourable. It is desirable that the silicone composition can be disposed between the photovoltaic cell layer 14 and the outer layer 16 without requiring the application of pressure, which may break, crack, or otherwise damage the photovoltaic cell layer 14 and/or the outer layer 16. The step of disposing the silicone composition between the photovoltaic cell layer 14
and the outer layer 16 may be carried out manually or may be carried out via appropriate equipment.

[0009] The silicone composition has a kinematic viscosity of from greater than 0 to less than 1,000, alternatively less than 500, alternatively less than 300, alternatively less than 100, alternatively less than 50, centistoke (cSt) at 25 °C. As readily understood in the art, kinematic viscosity of a fluid may be measured in accordance with ASTM D-445 (2011), entitled "Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)." The silicone composition may comprise any silicone composition having a kinematic viscosity less than 1,000 cSt at 25 °C which is capable of polymerizing in situ to form a siloxane (i.e., Si-O-Si) bond. The kinematic viscosity relates to the silicone composition prior to being polymerized and/or cross-linked. Accordingly, to achieve a kinematic viscosity of less than 1,000 cSt at 25 °C, the silicone composition generally comprises monomeric and/or oligomeric silanes, siloxanes, other organosilicon compounds, or combinations thereof.

[0010] In certain embodiments, the silicone composition comprises at least one monomeric cyclosiloxane. For purposes of clarity, the at least one monomeric cyclosiloxane is/are herein collectively referred to merely as "the monomeric cyclosiloxane," although the silicone composition may comprise more than one monomeric cyclosiloxane and various blends of different monomeric cyclosiloxanes.

[0011] Monomeric cyclosiloxanes are cyclic siloxanes which include repeating siloxane bonds and two monovalent groups, typically monovalent hydrocarbon groups, bonded to each silicon atom of the cyclosiloxanes. The monomeric cyclosiloxane may have the general formula \( \left( RIR_3SiO \right)_x \) where \( R^1 \), \( R^2 \), and \( R^3 \) independently selected from a substituted or unsubstituted hydrocarbyl group having from 1 to 10 carbon atoms and \( x \) is an integer of from 3 to 10. Specific examples of unsubstituted hydrocarbyl groups are alkyl groups, such as methyl groups, ethyl groups, n-propyl groups, 1-methylethyl groups, butyl groups, 1-methylpropyl groups, 2-methylpropyl groups, 1,1-dimethylethyl groups, pentyl groups, 1-methylbutyl groups, 1-ethylpropyl groups, 2-methylbutyl groups, etc.; alkenyl groups, such as vinyl groups, allyl groups, propenyl groups, hexenyl groups, etc.; cycloalkyl groups, such as cyclopentyl groups, cyclohexyl groups, methylcyclohexyl groups, etc.; aryl
groups, such as phenyl groups, naphthyl groups, etc.; alkaryl groups, such as tolyl
groups, xylyl groups, etc.; aralkyl groups, such as phenethyl groups, phenpropyl groups,
etc.; aralkenyl groups, such as styril groups, etc.; and alkynyl
groups, such as ethynyl groups, propynyl groups, etc. Substituted hydrocarbyl groups
include hydrocarbyl groups substituted with, for example, halogen atoms. One
example of a substituted hydrocarbyl group is a trifluoropropyl group. Typically, at
least 80% of all R\(^1\) and R\(^2\) are methyl groups or phenyl groups, with methyl groups
being more typical. Most typically, all or substantially all of R\(^1\) and R\(^2\) are methyl
groups.

**[0012]** When R\(^1\) and R\(^2\) are methyl groups, monomeric cyclosiloxanes are
generally referenced in the art as a numeral following the letter D, where the numeral
designates the number of silicon atoms in the particular monomeric cyclosiloxane. For
example, when R\(^1\) and R\(^2\) are methyl groups, a monomeric cyclosiloxane having
three silicon atoms is referred to as D\(_3\), a monomeric cyclosiloxane having four
silicon atoms is referred to as D\(_4\), a monomeric cyclosiloxane having five silicon
atoms is referred to as D\(_5\), etc. Accordingly, when the silicone composition comprises
the monomeric cyclosiloxane having the general formula (R\(^1\)R\(^2\)Si\(_2\)O\(_n\)), and when R\(^1\)
and R\(^2\) are methyl groups, the monomeric cyclosiloxane may be referred to as D\(_3\),
D\(_4\), D\(_5\), D\(_6\), D\(_7\), D\(_8\), D\(_9\), and/or D\(_{10}\). In these embodiments, the numeral following
the letter D also designates the number of \(-\text{Si(CH}_3\text{)}_2\text{O}\) repeating units in the
particular monomeric cyclosiloxane, and the letter D itself represents the \(-\text{Si(CH}_3\text{)}_2\text{O}\) unit. As introduced above, the monomeric cylosiloxane may include
substituted or unsubstituted hydrocarbyl groups other than methyl groups. In these
embodiments, there are other shorthand designations generally utilized in the art. As
but one example, when the monomeric cyclosiloxane includes three silicon atoms,
and when two of the silicon atoms include silicon-bonded methyl groups and the third
silicon atom includes silicon-bonded phenyl groups, the monomeric cyclosiloxane
may be referred to as D\(_2\)P, or D\(_{2}\)Ph, where D\(_2\) designates that two of the silicon
atoms have silicon-bonded methyl groups and P or Ph designates that the third silicon
atom has silicon-bonded phenyl groups.
Generally, the monomeric cyclosiloxane includes from 3 to 6 silicon atoms such that subscript x is typically from 3 to 6 in the general formula given above for the monomeric cyclosiloxane. Thus, when \( R^1 \) and \( R^2 \) are methyl groups, the monomeric cyclosiloxane is generally selected from \( D_3 \), \( D_4 \), \( D_5 \), and/or \( D_6 \). There are numerous monomeric cyclosiloxanes having various \( R^1 \) and \( R^2 \) groups and having from 3 to 6 silicon atoms, which are not exhaustively set forth herein. In embodiments in which the monomeric cyclosiloxane is \( D_3 \), \( D_4 \), \( D_5 \), and/or \( D_g \) and \( R^1 \) and \( R^2 \) are methyl, the monomeric cyclosiloxane can alternatively be referred to as hexamethylocyclotrisiloxane \( (D_3) \), octamethylcyclooctasiloxane \( (D_4) \), decamethylcyclopentasiloxane \( (D_5) \) and dodecamethylcyclohexasiloxane \( (D_g) \).

In embodiments in which the silicone composition comprises the monomeric cyclosiloxane, the monomeric cyclosiloxane is typically present in the silicone composition in an amount of from at least 80, alternatively at least 85, alternatively at least 90, alternatively at least 95, alternatively at least 99 percent by weight based on the total weight of the silicone composition. The amount of the monomeric cyclosiloxane present in the silicone composition may deviate from the ranges set forth above dependent upon whether the silicone composition includes solvent or other various additive components or compounds.

In embodiments in which the silicone composition comprises the monomeric cyclosiloxane, the silicone composition typically further comprises a polymerization catalyst. The monomeric cyclosiloxane may undergo ring-opening polymerization and the polymerization catalyst may be any polymerization catalyst which is suitable for facilitating the ring-opening polymerization of the monomeric cyclosiloxane. Such polymerization catalysts are well known in the art.

The ring-opening polymerization of the monomeric cyclosiloxane may be anionic or cationic. Anionic ring-opening polymerization of the monomeric cyclosiloxane is typically initiated by inorganic or organic bases. Specific examples of the polymerization catalyst for anionic ring-opening polymerization of the monomeric cyclosiloxane are silanolate compounds and metal hydroxides, such as alkali metal hydroxides. Cationic ring opening polymerization of the monomeric cyclosiloxane is typically initiated by protic acids or protic acids in combination with other acids or...
compounds, such as a protic acid in combination with a Lewis acid. Specific examples of the polymerization catalyst for cationic ring-opening polymerization of the monomeric cyclosiloxane are H2SO4, CF3SO3H, HClO4, CH3SO3H, etc.

[0017] In certain embodiments, the polymerization catalyst comprises a phosphazene base. Generally, any ionic or non-ionic phosphazene base is suitable for the purposes of the polymerization catalyst. Specific examples of phosphazene bases suitable for ring-opening polymerization of the cyclosiloxane include those described in U.S. Pat. Nos. 5,883,215, 6,284,859, 6,353,075, and 6,448,196, which are all herein incorporated by reference in their entireties.

[0018] Phosphazene bases generally include the following core structure \( \text{P} = \text{N} \) — \( \text{P} = \text{N} \), in which free N valencies are linked to hydrogen or hydrocarbon, i.e. form amino groups, and free P valencies are linked to amino groups. Phosphazene bases and routes for their synthesis have been described in the literature, for example in Schwesinger et al., Liebigs Ann. 1996, 1055-1081. Phosphazene bases are commercially available from various sources and suppliers.

[0019] The non-ionic phosphazene base typically has at least 3 phosphorous atoms per molecule. The phosphazene base may have the following general formula:

\[
\{(R_2^3 N)_3 \text{P} = \text{N} \} \cdot y \{(R_2^3 N)_{3-y} \text{P} = \text{N} \} \cdot \text{P} = \text{NR}^4
\]

wherein \( R^3 \) is independently selected from a hydrogen atom and a substituted or unsubstituted hydrocarbyl group, \( R^4 \) is selected from a hydrogen atom and a substituted or unsubstituted hydrocarbyl group, and \( y \) is 1, 2 or 3, most typically 2 or 3. Suitable examples of substituted and unsubstituted hydrocarbyl groups are set forth above with respect to \( R^1 \) and \( R^6 \). In the structure of the non-ionic phosphazene base, two \( R^3 \) groups bonded to the same N atom may be linked to complete a heterocyclic ring, such as a 5- or 6-membered ring. In certain embodiments, \( R^3 \) is a methyl group, \( R^4 \) is a tertiary butyl group or a tertiary octyl group, and \( y \) is 3.

[0020] The ionic phosphazene base typically has one of the following general formulas:

\[
\{(R_2^3 N)_3 \text{P} = \text{N} \} \cdot y \{(R_2^3 N)_{3-y} \text{P} = \text{N} \} \cdot \text{P} = \text{NR}^4 \} \cdot \{\text{A}^-\};
\]

\[
\{(R_2^3 N)_3 \text{P} = \text{N} \} \cdot y \{(R_2^3 N)_{3-y} \text{P} = \text{N} \} \cdot \text{P}^+ \{\text{A}^-\}; \text{ or}
\]
wherein R³ and R⁴ are as defined above, y' is 1, 2 or 3, y'' is 1, 2, 3 or 4, y''' is from 1 to 10, and A⁻ is an anion. In the structures of the ionic phosphazene bases above, two R³ groups bonded to the same N atom may be linked to complete a heterocyclic ring, such as a 5- or 6-membered ring.

[0021] The phosphazene base may be provided, obtained, or prepared in various forms. For example, the phosphazene base may be diluted in a hydrocarbon solvent, such as hexane or heptane, or dispersed in a silicone fluid, such as polydiorganosiloxanes. The solvent can be removed by evaporation under vacuum, and the catalyst dispersed in a silicone fluid to give a stable clear solution. The phosphazene base may alternatively be dissolved in water, or the phosphazene base may be provided in the absence of a solvent or other carrier.

[0022] The polymerization catalyst is present in the silicone composition in a catalytically effective amount. The phosphazene base may be generally present in the silicone composition in a relatively low proportion, for example from 2 to 200 ppm by weight, based on the total weight of the monomeric cyclosiloxane. This amount refers solely to the phosphazene base itself without regard to any solvent or other carrier in which the phosphazene base may be disposed. As readily understood in the art, the amount of the polymerization catalyst utilized is contingent on many factors, such as the desired speed at which the ring-opening polymerization of the monomeric cyclosiloxane progresses.

[0023] In certain embodiments in which the silicone composition comprises the monomeric cyclosiloxane, the silicone composition further comprises a branching agent. Ring-opening polymerization of the monomeric cyclosiloxane generally results in linear organopolysiloxanes. As such, a branching agent may be utilized in the silicone composition, which reacts during the ring-opening polymerization of the monomeric cyclosiloxane to impart branching within the encapsulant layer 12 formed from the silicone composition. The branching agent may also impart the encapsulant layer 12 formed from the silicon composition with a three-dimensional cross-linked...
network. To this end, the branching agent typically comprises a tri- or tetra-functional compound, such as a tri- or tetra-functional alkoxy silane.

[0024] The branching agent may have the general formula:

\[
\text{Si(OR}^3\text{)}_x \text{R}^6_{4-x},
\]

wherein \( R^5 \) is independently selected from a monovalent hydrocarbon group having from 1 to 4 carbon atoms, \( R^6 \) is independently selected from a substituted or unsubstituted hydrocarbyl group having from 1 to 10 carbon atoms, and \( z \) is 3 or 4. Specific examples of hydrocarbyl groups suitable for \( R^5 \) and \( R^6 \) include those set forth above for \( R^1 \) and \( R^8 \). One particular example of a branching agent particularly suitable for the silicone composition is tetraethoxysilane, which is also referred to as tetraethylorthosilicate, or TEOS.

[0025] Alternatively or in addition to the general formula above, the branching agent may comprise a silicone resin. Once specific example of a silicone resin suitable for the purposes of the branching agent is an MQ resin. MQ resins comprises M units, i.e., \( \text{RS}1\text{O3/2} \) units, where \( R \) may be an independently selected substituted or unsubstituted hydrocarbyl group or a hydroxy group, and \( Q \) units, i.e., \( \text{S1O4/2} \) units. The M and Q units may be present in the MQ resin in various molar ratios depending on the desired molecular weight of the MQ resin. M and Q units may be present in the MQ resin in a ratio ranging from 4:1 to 0.7:1. The MQ resin typically has a molecular weight of less than 20,000, which decreases as the ratio of M units relative to Q units increases.

[0026] When utilized in the silicone composition along with the monomeric cyclosiloxane, the branching agent is generally present in the silicone composition in an amount of no greater than 10 percent by weight based on the total weight of the silicone composition. The amount of the branching agent present in the silicone composition may deviate from the ranges set forth above dependent upon whether the silicone composition includes solvent or other various additive components or compounds.

[0027] In various embodiments in which the silicone composition comprises the monomeric cyclosiloxane, the silicone composition further comprises a chain terminating agent. A chain terminating agent generally provides at least one \( M \) unit,
i.e., an \( \text{R}^7 \text{SiO}_{1/2} \) unit, where \( \text{R}^7 \) is typically a hydrocarbyl group. The M unit terminates a polymer chain to prevent further chain group and/or polymerization at that location. Accordingly, the chain terminating agent may be employed in the silicone composition to selectively control the kinematic viscosity and/or degree of polymerization of the encapsulant layer 12 formed from the silicone composition.

[0028] In one embodiment, the chain terminating agent has the following average formula:

\[
\begin{array}{c}
\text{Z} \quad \text{Si} \quad \text{X} \quad \text{Si} \\
\text{R}^8 \quad \text{R}^9 \\
\text{R}^8 \quad \text{R}^9 \quad \text{y}
\end{array}
\]

where \( \text{Z} \) is a halogen atom, an alkoxy group having from 1 to 10 carbons, or a substituted or unsubstituted hydrocarbyl group having from 1 to 10 carbon atoms; \( \text{R}^8 \), \( \text{R}^9 \), and \( \text{R}^{10} \) are each independently a substituted or unsubstituted hydrocarbyl groups having from 1 to 10 carbon atoms; \( \text{X} \) is O or NH, and \( \text{y} \) ranges from 0 to 1.

[0029] The chain terminating agent may be, for example, a silane, a siloxane, or a silazane. Suitable silanes include, for example, triorganosilanes, such as halo-, alkoxy-, and carboxy- triorganosilanes. Specific examples of the silane or silazanes chain terminating agent are trimethylchlorosilane, trimethylmethoxysilane, hexamethyldisiloxane, diphenylmethylmethoxysilane, dimethylphenylmethoxysilane, diphenylmethyldisiloxane, hexamethyldisilazane, tetramethylidivinyldisiloxane, and hydrolyzates thereof. One specific example of a siloxane suitable for the purposes of the chain terminating agent is trimethyl endblocked polydimethylsiloxane. The chain terminating agent may be included in the silicone composition prior to disposing the silicone composition between the photovoltaic cell layer 14 and the outer layer 16. Alternatively, the chain terminating agent may be disposed between the photovoltaic cell layer 14 and the outer layer 16 during polymerization of the silicone composition, i.e., after disposing the silicone composition between the photovoltaic cell layer 14 and the outer layer 16. The chain terminating agent is typically utilized in an amount of from greater than 0 to 20 percent by weight based on the total weight of the silicone composition. The amount of the chain terminating agent present in the silicone composition may deviate from
the ranges set forth above dependent upon whether the silicone composition includes solvent or other various additive components or compounds.

[0030] In the embodiments described above where the silicone composition comprises the monomeric cyclosiloxane, the silicone composition may further comprise other various components, such as solvents, thixotropic agents, fillers, organopolysiloxane fluids, etc. The silicone composition comprising the monomeric cyclosiloxane may be solventless, i.e., substantially free from solvent other than any solvent that may be provided along with the polymerization catalyst. For purposes of this disclosure, the components described herein, e.g. the monomeric cyclosiloxane, the polymerization catalyst, and the branching agent, do not constitute a solvent, even if any of these components are capable of solubilizing any other components of the silicone composition. The silicone composition is typically free from conventional solvents, e.g. water, aliphatic and aromatic hydrocarbons, alcohols, etc. Said differently, solvent is typically not included in the silicone composition as a discrete component.

[0031] As introduced above, in certain embodiments, the silicone composition further comprises a filler. The filler may be coated with a fluorescent material. Alternatively, the fluorescent material may be dissolved in the filler. The fluorescent material may be fluorescent, luminescent, or phosphorescent.

[0032] Fluorescent, luminescent, or phosphorescent materials can absorb light in the blue or UV range and emit visible light. Accordingly, in some embodiments, the fluorescent material absorbs blue and/or ultraviolet light, and the fluorescent material emits visible and/or infrared light. Phosphorescent materials, which may also be referred to as phosphors, typically comprise a suitable host material and an activator material. The host materials are typically oxides, sulfides, selenides, halides or silicates of zinc, cadmium, manganese, aluminum, silicon, or various rare earth metals. The activators are added to prolong emission time.

[0033] Exemplary phosphors are copper-activated zinc sulfide (ZnS:Cu) and silver-activated zinc sulfide (ZnS:Ag). Other exemplary phosphorescent materials are zinc sulfide and cadmium sulfide (ZnS:CdS), strontium aluminate activated by europium (SrAlC\(^{3+}\)Eu), strontium titanium activated by praseodymium and aluminum (SrTiC\(^{3+}\):Pr,Al), calcium sulfide with strontium sulfide with bismuth ((Ca,Sr)S:Bi),

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copper and magnesium activated zinc sulfide (ZnS:Cu,Mg), or any combination thereof.

[0034] The invention method further comprises polymerizing the silicone composition in situ between the photovoltaic cell layer 14 and the outer layer 16, thereby forming the encapsulant layer 12 in the photovoltaic cell module 10. The step of polymerizing the silicone composition may vary dependent upon the silicone composition employed. Generally, it is desirable to polymerize the silicone composition in situ between the photovoltaic cell layer 14 and the outer layer 16 at ambient conditions or at slightly elevated temperatures such that the photovoltaic cell layer 14 and the outer layer 16 need not be subjected to high (e.g. greater than 100 °C) temperatures or other polymerization techniques, such as radiation. Polymerization of the silicone composition is in situ because the silicone composition is disposed between the photovoltaic cell layer 14 and the outer layer 16 during polymerization of the silicone composition.

[0035] Polymerizing the monomeric cyclosiloxane can be carried out in the presence of water, a silanol or an alcohol, or in the absence of any of these compounds. Apart from when non-ionic phosphazene bases are utilized as the polymerization catalyst, water is not generally utilized for initiating polymerization of the silicone composition. However, when present in the silicone composition, water is typically utilized in an amount of from 0.5 to 10 mols per mol of the polymerization catalyst. If present, the silanol, for example a trialkyl silanol, or alcohol, for example an alcohol having 1 to 8 carbon atoms, may be utilized in similar amounts.

[0036] In embodiments in which the silicone composition comprises the monomeric cyclosiloxane, polymerizing the silicone composition can be carried out at a wide range of temperatures. For example, the silicone composition may be polymerized at ambient temperature and pressure. Alternatively, the silicone composition may be polymerized at ambient pressure but at a temperature greater than ambient temperature, such as from greater than ambient temperature to 300, alternatively from greater than ambient temperature to 250, alternatively from greater than ambient temperature to 200, alternatively from greater than ambient temperature to 150, alternatively from greater than ambient temperature to 100, alternatively from greater than ambient temperature to 80, alternatively from greater than ambient temperature to 60, °C. The time during which the silicone composition is polymerized
is contingent on many variables, such as the particular polymerization catalyst utilized, the amount of the particular polymerization catalyst employed, and the desired physical properties of the encapsulant layer 12 formed from polymerizing the silicone composition. The time during which the silicone composition is polymerized in situ may be from greater than 0 to 504, alternatively from 12 to 336, alternatively from 24 to 168, hours. Generally, the silicone composition is polymerized while at least partially exposed to ambient air, i.e., the silicone composition is typically not fully enclosed during the step of polymerizing the silicone composition. Polymerizing the silicone composition may be supplemented by additional curing methodologies, such as γ-radiation.

[0037] The encapsulant layer 12 formed from the silicone composition comprising the monomeric cyclosiloxane is generally referred to as a gum. The cross-link density and dynamic viscosity of the encapsulant layer 12 is contingent on many factors, including the parameters at which the silicone composition is cured (e.g. temperature, time, etc.) as well as the presence or absence of the branching agent. Typically, the encapsulant layer 12 formed from the silicone composition when the silicone composition comprises the monomeric cyclosiloxane has a dynamic viscosity of at least 50, alternatively at least 1,000, alternatively at least 10,000, alternatively at least 100,000 centiPoise (or mPa-s).

[0038] Regardless of the particular silicone composition employed in the method, the encapsulant layer 12 formed from the silicone composition is substantially transparent to allow for sunlight, including ultraviolet light, to substantially pass through the encapsulant layer 12. In particular, the encapsulant layer 12 has a light transmittance of at least 70 percent as determined using UV/Vis spectrophotometry using ASTM E424-71. In one embodiment, the encapsulant layer 12 has a light transmittance of at least 80 percent. In an alternative embodiment, the encapsulant layer 12 has a light transmittance of at least 90 percent. In still another embodiment, the encapsulant layer 12 has a light transmittance of approximately 100 percent.

[0039] As introduced above, the silicone composition is disposed and polymerized in situ between the photovoltaic cell layer 14 and the outer layer 16. The photovoltaic cell layer 14 and the outer layer 16 are conventional layers of photovoltaic cell modules. Accordingly, the outer layer 16 may be any outer layer known to one of skill in the art for photovoltaic cell modules, and, similarly, the
photovoltaic cell layer 14 may be any photovoltaic cell layer known to one of skill in the art for photovoltaic cell modules.

[0040] In particular, the outer layer 16 is substantially transparent to allow for sunlight, including ultraviolet light, to substantially pass through the outer layer 16. The outer layer 16 has a light transmittance of at least 70 percent as determined using UV/Vis spectrophotometry using ASTM E424-71. In one embodiment, the outer layer 16 has a light transmittance of at least 80 percent. In an alternative embodiment, the outer layer 16 has a light transmittance of at least 90 percent. In still another embodiment, the outer layer 16 has a light transmittance of approximately 100 percent.

[0041] In certain embodiments, the outer layer 16 and the encapsulant layer 12 have similar refractive index values. In particular, the outer layer 16 and the encapsulant layer 12 have refractive index values within 0.1, alternatively within 0.08, alternatively within 0.06, alternatively within 0.04, alternatively within 0.02, alternatively within 0.01 of one another.

[0042] The outer layer 16 is typically rigid and stiff. Alternatively, the outer layer 16 may comprise rigid and stiff segments while simultaneously including soft and flexible segments. In one embodiment, the outer layer 16 comprises glass. The glass may be, for example, soda lime glass. In another embodiment, the outer layer 16 comprises a polymer. The polymer may be selected from the group of, but is not limited to, polyimides; acrylics such as polymethylmethacrylate; polycarbonate; ethylene-vinyl acetate copolymers; fluoropolymers, such as ethylene tetrafluoroethylene and polyvinyl fluoride; polyalkylene terephthalates, such as polyethylene terephthalate or polybutylene terephthalate; and combinations thereof. Such polymers may be coated with silicon and oxygen based materials (SiO$_x$).

[0043] The photovoltaic cell layer 14 is for converting light energy into electricity via the photovoltaic effect. Specifically, the photovoltaic cell layer 14 comprises a photovoltaic cell, which converts light energy into electricity. The photovoltaic cell may comprise large-area, single-crystal, single layer p-n junction diodes. These photovoltaic cells are typically made using a diffusion process with silicon wafers. Alternatively, the photovoltaic cell may include thin epitaxial deposits of (silicon) semiconductors on lattice-matched wafers. In this embodiment, the photovoltaic cell layer 14 may be classified as either space or terrestrial and typically has AM0
efficiencies of from 7 to 40%. Further, the photovoltaic cell may comprise quantum well devices such as quantum dots, quantum ropes, and the like, and also include carbon nanotubes. Without intending to be limited by any particular theory, it is believed that these types of photovoltaic cells can have up to a 45% AMO production efficiency. Still further, the photovoltaic cell may comprise mixtures of polymers and nanoparticles that form a single multi-spectrum layer which can be stacked to make multi-spectrum solar cells more efficient and less expensive.

[0044] Alternatively, the photovoltaic cell of the photovoltaic cell layer may comprise a CIS-based solar absorber layer comprising copper, indium, and selenium. In certain embodiments in which the photovoltaic cell comprises the CIS-based solar absorber layer, the CIS-based solar absorber layer may further comprise a metal selected from the group of gallium, aluminum, boron, tellurium, sulfur, and combinations thereof.

[0045] Specific examples of the photovoltaic cell of the photovoltaic cell layer 14 include amorphous silicon, monocrystalline silicon, polycrystalline silicon, microcrystalline silicon, nanocrystalline silica, cadmium telluride, copper indium/gallium selenide/sulfide (CIGS), gallium arsenide, polyphenylene vinylene, copper phthalocyanine, carbon fullerenes, and combinations thereof in ingots, ribbons, thin films, and/or wafers. The photovoltaic cell layer 14 may also comprise light absorbing dyes such as ruthenium organometallic dyes. In certain embodiments, the photovoltaic cell layer 14 comprises monocrystalline and/or polycrystalline silicon. In other embodiments, the photovoltaic cell layer 14 comprises copper indium/gallium selenide/sulfide (CIGS).

[0046] The photovoltaic cell layer 14 may further comprise a support layer for providing rigidity to the photovoltaic cell. For example, the photovoltaic cell may be disposed on the support layer to provide the photovoltaic cell layer 14, which has increased rigidity as compared to the photovoltaic cell itself. The support layer may comprise the same material as the outer layer 16 or a different material than the outer layer 16.

[0047] The photovoltaic cell layer 14 may have a first shape extending between a first end and a second end and the outer layer 16 may have a second shape substantially identical to the first shape of the photovoltaic cell layer 14. As shown in Figure 2, the first and second shapes of the photovoltaic cell layer 14 and the outer
layer 16, respectively, may be cylindrical. In these embodiments, the photovoltaic cell layer 14 has an inner and outer diameter and the outer layer 16 has an inner and outer diameter. The inner diameter of the outer layer 16 is generally greater than the outer diameter of the photovoltaic cell layer 14 such that when the photovoltaic cell layer 14 is disposed in the outer layer 16, the photovoltaic cell layer 14 and the outer layer 16 are concentric cylinders which define a space therebetween for the silicone composition to form the encapsulant layer 12, as shown in Figure 1. In these embodiments, the difference between the outer diameter of the photovoltaic cell layer 14 and the inner diameter of the outer layer 16 defines a thickness of the encapsulant layer 12 formed from the silicone composition. Specifically, half of the difference between the outer diameter of the photovoltaic cell layer 14 and the inner diameter of the outer layer 16 is equivalent to the thickness of the encapsulant layer 12. Generally, the thickness of the encapsulant layer 12 is from greater than 0 to 3, alternatively from 1 to 2.5, alternatively from 1.75 to 2.25, mm. The inner and outer diameters of the photovoltaic cell layer 14 and the outer layer 16 may vary dependent upon the desired size of the photovoltaic cell module 10. The first and second shapes of the photovoltaic cell layer 14 and the outer layer 16 may be shapes other than cylindrical without departing from the scope of this invention. For example, the first and second shapes of the photovoltaic cell layer 14 and the outer layer 16 may be rectangular, octagonal, elliptical, etc. Further, the first and second shapes of the photovoltaic cell layer 14 and the outer layer 16 may be other than substantially identical to one another. For example, the first shape of the photovoltaic cell layer 14 may be rectangular whereas the second shape of the outer layer 16 may be cylindrical. In this embodiment, the encapsulant layer 12 has a non-uniform thickness.

[0048] The photovoltaic cell module 10 further includes a base layer which couples the outer layer 16 and the photovoltaic cell layer 14. Specifically, the base layer is typically coupled to a bottom of the outer layer 16 and the photovoltaic cell layer 14 such that the silicone composition can be disposed between the base layer and the photovoltaic cell layer 14 from a top of the photovoltaic cell module 10 without leaking from the bottom of the photovoltaic cell module 10. The base layer may comprise any suitable material for preventing the silicone composition from leaking form between the outer layer 16 and the photovoltaic cell layer 14 prior to polymerizing the silicone composition to form the encapsulant layer 12. Similarly, the
photovoltaic cell module 10 generally includes a top layer disposed opposite the base layer, i.e., disposed on the top of the photovoltaic cell module 10, which seals the encapsulant layer 12 between the top and base layers and between the outer layer 16 and the photovoltaic cell layer 14. The top layer may be the same as or different from the base layer. The top layer may be disposed on the top of the photovoltaic cell module 10 prior to or after polymerizing the silicone composition. Typically, the top layer is not disposed on the top of the photovoltaic cell module 10 until the silicone composition is polymerized such that the silicone composition is polymerized while at least partially exposed to ambient air, as introduced above. In embodiments in which the silicone composition comprises the branching agent, the branching agent may react, e.g., hydrolyze, when in contact with ambient moisture prior to reacting with the components of the silicone composition or simultaneously while reacting with the components of the silicone composition.

[0049] Specific examples of the preparation and configuration of cylindrical photovoltaic cell modules are disclosed in U.S. Publ. Pat. Appln. No. 2009/0014055, which is herein incorporated by reference in its entirety. This application discloses various components that are generally included in such cylindrical photovoltaic cell modules which are not expressly described herein. In particular, this application discloses various aspects of the electrical connections and electrodes of cylindrical photovoltaic cell modules, as well as the configuration of the photovoltaic cell layer.

[0050] Once the encapsulant layer 12 is polymerized in situ between the photovoltaic cell layer 14 and the outer layer 16, the photovoltaic cell module 10 formed therefrom may be utilized. For example, the photovoltaic cell module 10 may be utilized individually, or the photovoltaic cell module 10 may be utilized in an array with a plurality of photovoltaic cell modules, as readily understood in the art. Because the encapsulant layer 12 formed from the silicone composition is polymerized, if the outer layer 16 is damaged during use of the photovoltaic cell module 10, the encapsulant layer 12 generally does not leak or otherwise escape from the photovoltaic cell module 10, which can have deleterious effects relative to the output and efficiency of the photovoltaic cell module 10.

[0051] One or more of the values described above may vary by ± 5%, ± 10%, ± 15%, ± 20%, ± 25%, etc. so long as the variance remains within the scope of the disclosure. Unexpected results may be obtained from each member of a Markush
group independent from all other members. Each member may be relied upon individually and or in combination and provides adequate support for specific embodiments within the scope of the appended claims. The subject matter of all combinations of independent and dependent claims, both singly and multiply dependent, is herein expressly contemplated. The disclosure is illustrative including words of description rather than of limitation. Many modifications and variations of the present disclosure are possible in light of the above teachings, and the disclosure may be practiced otherwise than as specifically described herein.

[0052] The following examples illustrate, and do not limit the scope of, the invention.

[0053] Various silicone compositions are prepared according to this invention. In particular, 19 silicone compositions comprising at least one monomeric cyclosiloxane are prepared. Tables 1 and 2 illustrative the various components and relative amounts of the various components in the 19 silicone compositions.
<table>
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<tr>
<th>Trial</th>
<th>Monomeric Cyclosiloxane</th>
<th>Amount (g)</th>
<th>Polymerization Catalyst</th>
<th>Amount (μL)</th>
<th>μmols OH/kg</th>
<th>Branching Agent</th>
<th>Amount (g)</th>
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<td>1</td>
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<td>--</td>
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<td>--</td>
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[0055] Branching Agent 1 comprises tetraethylorthosilicate.

[0056] Branching Agent 2 comprises tetrakis(dimethylvinylsiloxy)silane.

Polymerization Catalyst 1 comprises an ionic phosphazene base catalyst.
To simulate cylindrical photovoltaic cell modules, a glass test tube is disposed in an inverted position into a glass cylinder. The glass cylinder has an inner diameter of 26.6 mm. The glass test tube has an outer diameter of 24.9 mm. The glass cylinder is representative of the outer layer of the photovoltaic cell module, and the glass test tube is representative of the photovoltaic cell layer of the photovoltaic cell module.

Each of the 19 silicone compositions is disposed in a glass cylinder to form encapsulant layers between the respective glass cylinders and glass test tubes. Each of the encapsulant layers has a diameter of 0.85 mm. The encapsulant layers were cured according to the parameters below in Tables 3 and 4. Viscosities of the respective encapsulant layers were measured. Viscosities of those encapsulant layers which were fluids were measured via a Brookfield rheometer at 25 °C. Viscosities of those encapsulant layers which were gums were measured via a biconical rheometer at 30 °C, 1.667 Hz and 13.95% strain. Viscosities of the encapsulant layers were measured at particular intervals to illustrate the change in kinematic viscosity over time, i.e., as the silicone compositions polymerized to form the encapsulant layers. In addition, the appearance of the encapsulant layer was visually inspected to determine clarity. In tables 3 and 4 below, "clear" indicates that the particular encapsulant layer was substantially transparent, i.e., not hazy or cloudy, upon visual inspection. Conversely, "hazy" indicates that the particular encapsulant layer was translucent or otherwise not substantially transparent. In the event that a desirable viscosity was obtained after 7 days (e.g. in trials 3-5), additional testing of physical properties was not conducted after 14 days, as noted in Table 3 below. The initial curing parameters for each trial are set forth in column 2 of Table 3. After 7 days, in situ polymerization...
continues at ambient conditions, even for those trials in which the initial curing parameters include a temperature greater than room temperature (e.g. 40 °C).

[0060] Table 3:

<table>
<thead>
<tr>
<th>Trial</th>
<th>Initial Curing Parameters</th>
<th>Physical Properties of Encapsulant Layer</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>3 days</td>
</tr>
<tr>
<td>1</td>
<td>40 °C for 7 days</td>
<td>Clear</td>
</tr>
<tr>
<td>2</td>
<td>40 °C for 7 days</td>
<td>Clear</td>
</tr>
<tr>
<td>3</td>
<td>40 °C for 7 days</td>
<td>Clear</td>
</tr>
<tr>
<td>4</td>
<td>40 °C for 7 days</td>
<td>Clear</td>
</tr>
<tr>
<td>5</td>
<td>40 °C for 7 days</td>
<td>Clear</td>
</tr>
<tr>
<td>6</td>
<td>30 °C for 7 days</td>
<td>Clear</td>
</tr>
<tr>
<td>7</td>
<td>30 °C for 7 days</td>
<td>Clear</td>
</tr>
<tr>
<td>8</td>
<td>30 °C for 7 days</td>
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<tr>
<td>9</td>
<td>30 °C for 7 days</td>
<td>Clear</td>
</tr>
<tr>
<td>10</td>
<td>room temperature</td>
<td>Little reaction</td>
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<tr>
<td>11</td>
<td>40 °C for 7 days</td>
<td>Some reaction</td>
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<tr>
<td>12</td>
<td>40 °C for 7 days</td>
<td>Some reaction</td>
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<td>13</td>
<td>40 °C for 7 days</td>
<td>Clear</td>
</tr>
<tr>
<td>14</td>
<td>40 °C for 7 days</td>
<td>Clear</td>
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<tr>
<td>15</td>
<td>30 °C for 7 days</td>
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[0061] Table 4:

<table>
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<th>Trial</th>
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<tr>
<td></td>
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<td>16</td>
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<tr>
<td>18</td>
<td>40 °C for 7 days</td>
<td>No reaction</td>
</tr>
<tr>
<td>19</td>
<td>40 °C for 7 days</td>
<td>No reaction</td>
</tr>
</tbody>
</table>

[0062] The invention has been described in an illustrative manner, and it is to be understood that the terminology which has been used is intended to be in the nature of words of description rather than of limitation. Obviously, many modifications and variations of this invention are possible in light of the above teachings. The invention may be practiced otherwise than as specifically described.
CLAIMS

What is claimed is:

1. A method of forming an encapsulant layer for a photovoltaic cell module comprising a photovoltaic cell layer and an outer layer spaced from the photovoltaic cell layer, said method comprising the steps of:

   disposing a silicone composition having a kinematic viscosity of from greater than 0 to less than about 1,000 centistoke (cSt) at 25 °C between the photovoltaic cell layer and the outer layer; and

   polymerizing the silicone composition in situ between the photovoltaic cell layer and the outer layer, thereby forming the encapsulant layer in the photovoltaic cell module.

2. A method as set forth in claim 1 wherein the silicone composition has a kinematic viscosity of from greater than 0 to less than about 300 cSt at 25 °C.

3. A method as set forth in any preceding claim wherein the silicone composition has a kinematic viscosity of from greater than 0 to less than about 100 cSt at 25 °C.

4. A method as set forth in any preceding claim wherein the silicone composition comprises at least one monomeric cyclosiloxane.

5. A method as set forth in claim 4 wherein the at least one monomeric cyclosiloxane has the general formula (R^1R^2Si02)_x, wherein R^1 and R^2 are independently selected from a substituted or unsubstituted hydrocarbyl group having from 1 to 10 carbon atoms and x is an integer of from 3 to 10.

6. A method as set forth in claim 4 wherein the at least one monomeric cyclosiloxane comprises at least one of hexamethylocyclotrisiloxane (D3), octamethylocyclotetrasiloxane (D4), decamethylocyclopentasiloxane (D5) and dodecamethylocyclohexasiloxane (D6).

7. A method as set forth in any one of claims 4-6 wherein the silicone composition further comprises a catalytically effective amount of a polymerization catalyst.

8. A method as set forth in claim 7 wherein the polymerization catalyst comprises a phosphazene base.
9. A method as set forth in claim 8 wherein the phosphazene base has a general formula selected from:

\[
((R^3_2N)_3P=N-)_y(R^3_2N)_3P=NR^4;
\]

\[
\{((R^3_2N)_3P=N-)_y(R^3_2N)_3P=N(H)R^4 \}^+ \{A^-\};
\]

\[
\{((R^3_2N)_3P=N-)_y''(R^3_2N)_4-y''''P \}^+ \{A^-\};
\]

\[
\{\substack{\text{(NR)}^4 \text{P} \equiv \text{N} \left( \begin{array}{c} \vdots \\ \vdots \end{array} \right) \text{P}^+ (\text{NR})^4 \text{P}^{-y''''} } \}
\]

wherein \(R^3\) is independently selected from a hydrogen atom and a substituted or unsubstituted hydrocarbyl group and two \(R^3\) groups bonded to the same N atom may be linked to complete a heterocyclic ring, \(R^4\) is selected from a hydrogen atom and a substituted or unsubstituted hydrocarbyl group, \(y\) is 1, 2 or 3, \(y'\) is 1, 2 or 3, \(y''\) is 1, 2, 3 or 4, \(y'''\) is from 1 to 10, and \(A^-\) is an anion.

10. A method as set forth in any one of claims 4-9 wherein the silicone composition further comprises a branching agent.

11. A method as set forth in claim 10 wherein the branching agent has the general formula:

\[
\text{Si}(\text{OR})^5_z \text{R}^6_{4-x},
\]

wherein \(R^5\) is independently selected from a monovalent hydrocarbon group having from 1 to 4 carbon atoms, \(R^6\) is independently selected from a substituted or unsubstituted hydrocarbyl group having from 1 to 10 carbon atoms, and \(z\) is 3 or 4.

12. A method as set forth in any one of claims 4-11 wherein the silicone composition further comprises a chain terminating agent having the following average formula:

\[
\text{Z-Si}^\text{8} \left[ \text{R}^8 \right] \left[ \text{X-Si}^\text{9} \right] \left[ \text{R}^9 \right] \text{R}^{10},
\]
where Z is a halogen atom, an alkoxy group having from 1 to 10 carbons, or a substituted or unsubstituted hydrocarbyl group having from 1 to 10 carbon atoms; R^9, R^9, and R^10 are each independently a substituted or unsubstituted hydrocarbyl groups having from 1 to 10 carbon atoms; X is O or NH, and y ranges from 0 to 1.

13. A method as set forth in any preceding claim wherein the photovoltaic cell layer has an inner and outer diameter and the outer layer has an inner and outer diameter such that the inner diameter of the outer layer is greater than the inner diameter of the photovoltaic cell layer.

14. A method as set forth in any preceding claim wherein the photovoltaic cell layer and the outer layer are cylindrical.

15. A method as set forth in any preceding claim wherein the photovoltaic cell layer comprises copper indium gallium diselenide.

16. A method as set forth in any preceding claim wherein the outer layer is substantially transparent.

17. A method as set forth in any preceding claim wherein the outer layer comprises glass.

18. A method as set forth in any preceding claim wherein the encapsulant layer formed from the silicone composition is substantially transparent.

19. A method as set forth in any preceding claim wherein the silicone composition is solventless.

20. A method of forming an encapsulant layer for a cylindrical photovoltaic cell module comprising a photovoltaic cell layer having an inner and outer diameter and further comprising an outer layer spaced from the photovoltaic cell layer and having an inner and outer diameter such that the inner diameter of the outer layer is greater than the inner diameter of the photovoltaic cell layer, said method comprising the steps of:

   disposing a silicone composition having a kinematic viscosity of from greater than 0 to less than about 1,000 centistoke (cSt) at 25 °C between the photovoltaic cell layer and the outer layer; and

   polymerizing the silicone composition in situ between the photovoltaic cell layer and the outer layer, thereby forming the encapsulant layer in the cylindrical photovoltaic cell module.
INTERNATIONAL SEARCH REPORT

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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<td>JP 2008 077874 A (SHINETSU POLYMER CO) 3 April 1 2008 (2008-04-03) abstract</td>
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Further documents are listed in the continuation of Box C.

* 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 application or patent but published on or after the international filing date
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   *O* document referring to an oral disclosure, use, exhibition or other means
   *P* document published prior to the international filing date but later than the priority date claimed

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

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

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

*"Z"* document member of the same patent family

Date of the actual completion of the international search: 18 March 2013

Date of mailing of the international search report: 25/03/2013

Name and mailing address of the ISA:
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax. (+31-70) 340-3016

Authorized officer: Schmi dt, Helmut
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