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(54) **Title:** SEALANT COMPOSITION

(57) **Abstract:** The present invention relates to a sealant composition for insulation of devices that are sensitive to the penetration of moisture from the external environment, comprising: - ethylene-octene copolymers; - a maleic anhydride modified polyolefin; - an ethylene-vinyl acetate copolymer; - at least one inert filler; - at least one moisture scavenger; - at least one stabilizing or antioxidant preserving agent.



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SEALANT COMPOSITION

The present invention relates to a sealant composition for the isolation of devices that are sensitive to permeation of moisture from the external environment.

5 It is well known that the insulating structures for moisture-sensitive devices are made with the aid of sealants compositions having a low rate of water vapor transmission.

In particular, it is known that the functionality of photovoltaic panels may be reduced in the event of permeation of moisture inside the panel. Thus, to prevent such
10 permeation, insulating structures for photovoltaic devices are known, which comprise a plurality of plates, made of glass or other moisture impervious material, which are joined at the edge zone by means of a spacer made of metallic material. Between the sides of the spacer facing the glass plates and the inner surfaces of the plates a sealant composition is employed, having the purpose of forming a barrier against the entrance
15 of the molecules of moisture within the photovoltaic panel. Sealant compositions used in photovoltaic panels, as well as in other devices sensitive to moisture, are subjected to thermal cycles, for example in the steps of the manufacturing processes of the panels or devices. Therefore, obtaining formulations with thermodynamic stability up to temperatures of 120-130 ° C is an advantage.

20 The known sealant compositions generally include olefin polymers modified with silanes as adhesion promoters.

International Publication WO2009/036752 describes a primary sealant composition comprising:

a) from 30% to 60% by weight, preferably from 40% to 50% by weight of olefin
25 polymers having number average molecular weight between 400 and 600,000 D, preferably between 5,000 and 300,000 D;

b) from 2% to 35% by weight, preferably from 5% to 25% by weight of a modified polymer;

c) from 5% to 40% by weight, preferably from 10% to 30% by weight of inert
30 fillers;

d) from 5% to 25% by weight, preferably from 10% to 15% by weight of moisture

sorbers, and

e) from 0% to 3% by weight of preservatives, in particular antioxidants agents or UV-rays protecting agents.

As olefinic polymers of high molecular weight, the use of polyisobutylene, polybutene, butyl rubber (polyisobutylene-isoprene), block copolymers of styrene, in particular SBS, SIS, SEBS, SEPS, SIBS, SPIS, also in modified form and copolymers and / or terpolymers of amorphous α -olefins is described.

As modified polymers, the use of polyolefins modified with silanes is described.

International Publication WO2011/047185 describes a sealant composition for photovoltaic devices having the following composition:

a) unsaturated or reactive polyolefins or combinations thereof in an amount from about 10% to 80% by weight with respect to the composition;

b) olefinic polymers or combinations thereof in an amount from about 5% to about 80% by weight with respect to the composition;

c) at least one filler in an amount from about 10% to about 60% by weight with respect to the total composition;

d) at least a moisture sorber in an amount from about 2.5% to about 25% by weight with respect to the total composition, and

e) at least one preserving agent comprising an antioxidant and/or a UV stabilizer in an amount from about 0.1% to about 3% by weight of the total composition.

The composition preferably further comprises a polymer modified with silanes in amounts of from 5% to 30% by weight of the total composition.

However, the magnitude of the effect of promoting adhesion generated from the polymers modified with silanes depends on the other components of the sealant composition as well as by the materials to be sealed. Therefore, the sealant compositions comprising polymers modified with silanes have a limited applicability in relation to the materials of destination and they require special caution with regard to their storage.

Furthermore, despite the efforts that were made so far, the need for a sealant composition having a high thermal stability and a low rate of water vapor transmission (MVT) continues to exist.

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The purpose of the present invention is therefore to provide a sealant composition free from the above mentioned drawbacks and having a high thermal stability and a low rate of water vapor transmission (MVT). Said object is achieved with a sealant composition whose main features are specified in the first claim, a use whose features
5 are specified in claim 13, and a solar module whose characteristics are specified in claim 15. Other features of the composition, the use and the module are specified in the remaining claims.

The composition according to the present invention comprises:

- a maleic anhydride modified polyolefin;
- 10 - at least one ethylene-octene copolymer;
- an ethylene-vinyl acetate copolymer;
- at least an inert filler;
- at least a moisture sorber, and
- at least a stabilizing or antioxidant preserving agent.

15 Preferably, in the composition according to the present invention the above mentioned components sum up to at least 95% of the weight of the overall composition to be used as a sealant in the production process of a device sensitive to moisture.

The inventors have found that the selection of above indicated components, and in particular the combination of a polyolefin modified with maleic anhydride and an
20 ethylene octane copolymer, allows to obtain a composition having an excellent sealant effectiveness regardless of the presence of polyolefins modified with silanes. According to one aspect of the invention, therefore, the composition object of the present invention does not include polyolefins modified with silanes.

Furthermore, the compositions according to the present invention show a high
25 thermal stability and a low rate of water vapor transmission (WVT).

Furthermore, the presence of an ethylene-vinyl acetate copolymer induces an increase in adhesion properties following the application of a compression force even after cooling of the adhesive sealant, resulting in improved performances as tacking and pressure sensitive adhesive.

30 In the composition according to the present invention the weight ratio between the amount of said ethylene-octene copolymer and said polyolefin modified with maleic

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anhydride is advantageously between 1:1 and 10:1, more preferably between 3:1 and 8:1, still more preferably between 4:1 and 6:1.

Preferably, said polyolefin modified with maleic anhydride is a copolymer of polyethylene/polypropylene grafted with maleic anhydride having an index MFI (acronym for "melt flow index") greater than 1 g/10 min and a density between 0.87 and 0.96 g / cc. The MFI index is a parameter that identifies the fluidity of the polymeric material in the molten state at a specific temperature and with a defined applied pressure and which can be evaluated in accordance with the ISO 1133 international procedure, similarly to the density of the same compositions generally evaluated in accordance with the international ASTM D 792.

Preferably said ethylene-octene copolymers are characterized by a degree of crystallinity between 10 and 35%, more preferably between 15 and 25%, a density between 0.86 and 0.90 g / cc and an MFI index equal to or greater than 5 g/10 min.

Preferably, said ethylene-vinyl acetate copolymer has a high content of vinyl acetate (greater than 30% by weight) and has an MFI index higher than 30 g/10 min.

In one alternative embodiment the above mentioned ethylene-octene copolymer is used in combination with a second ethylene-octene copolymer having higher MFI index, preferably greater than 30 g/10 min

As inert fillers, the composition according to the present invention may comprise gypsum, silicates, silicon oxides, titanium oxide and carbon black. An alternative composition according to the invention comprises a mixture of talc and carbon black. In a particularly advantageous way, is used a mixture of talc and carbon black in a proportion by weight of between 6:1 and 8:1, more preferably between 2:1 and 4:1..

As moisture sorbers, the compounds commonly used in the sealant compositions for isolation of devices can be used, for example powders of one or more compounds selected from the group consisting of alkaline earth metal oxides and aluminosilicates. Alkaline earth metal oxides are preferably selected from the oxides of lithium, calcium, strontium, barium, magnesium. Preferably, as moisture sorbers calcium oxide and magnesium oxide are used.

The preservatives preferably used in the composition according to the present invention are selected from the group consisting of sterically hindered phenols, hindered

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amines and mercapto compounds, whereas benzophenone and benzotriazole might be commercially available antioxidant preserving agent suitable to be used in the composition according to the present invention.

According to a preferred embodiment of the invention, the sealant composition
5 comprises:

- said polyolefin modified with maleic anhydride in an amount between 5% and 20% by weight, more preferably between 8% and 10% by weight, relative to the total weight of the composition;

- said ethylene-octene copolymer in an amount comprised between 40% and 60%
10 by weight, more preferably between 50% and 55% by weight, relative to the total weight of the composition;

- said ethylene-vinyl acetate copolymer in an amount comprised between 0.5% and 5% by weight, more preferably between 1% and 4% by weight, relative to the total weight of the composition;

- said at least one inert filler in an amount comprised between 1% and 30% by
15 weight, more preferably between 1% and 4% by weight, relative to the total weight of the composition;

- said at least one moisture absorbent in a quantity comprised between 20% and 40% by weight, more preferably between 25% and 35% by weight relative to the total
20 weight of the composition, and

- said at least one preserving agent in an amount between 0.5% and 5% by weight, more preferably between 1% and 3% by weight, relative to the total weight of the composition.

The composition according to the present invention advantageously further
25 comprises at least one flame retardant, preferably consisting of magnesium hydroxide.

Said flame retardant is present in the composition according to a preferred embodiment of the invention in an amount between 0.5% and 3% by weight relative to the total weight of the composition.

The sealant composition according to the invention can be formulated in a unique
30 mixture that is usable as such, or in two pre-mixtures to be mixed immediately before use by the end user.

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The sealant composition according to the present invention is advantageously used to manufacture insulation structures for any device sensitive to moisture, such as for example electronic devices, photosensitive devices, medical devices with particular reference to pacemakers, organic electroluminescent devices, with particular reference to OLED and OLET devices, solid state photoelectrochemical solar cells (SSPECs) and dye sensitized solar cells (DSSCs), as well as solar panels comprising at least one photovoltaic cell.

In one aspect, the invention further relates to a solar panel comprising at least one photovoltaic cell interposed between at least a first substrate and at least a second substrate, for example a sheet of glass, metal or other material impervious to moisture. A composition according to the present invention is positioned as a sealant between said first substrate and said second substrate, as well as any additional elements such as a spacer made of metallic material.

The invention is illustrated by the following non-limiting examples:

EXAMPLE 1

A polymer composition according to the present invention was obtained from a mixture of DOW Engage ® 8411 type polyethylene (1-octene), a DOW Amplify™ TY 1351 type polyolefin modified with maleic anhydride, a Arkema Evatane ® 33-45 type random copolymer of ethylene-vinyl acetate produced through radical high-pressure polymerization, and a ethyleneglycol bis [3,3-bis (3-tert-butyl-4-hydroxyphenyl) butyrate] type preserving agent, in proportions by weight, respectively, of 100:19:6:3.

The thus obtained mixture was heated to a temperature of about 220°C in a thermostated chamber containing two counterrotating tools set to a constant rotational speed (twin-screw system) and kept in rotation for 3 minutes.

Then, a mixture of talc and carbon black in 10:1 ratio and a mixture of CaO and MgO in a 2:1 ratio, respectively for amounts of 6% and 28% compared to the total weight of the thus obtained composition, were added. The mixture was then maintained in rotation at constant speed and a flame retardant in an amount corresponding to 2% by weight with respect to the composition was then added. The temperature was increased up to 245°C.

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The composition was cooled and subjected to characterization by differential scanning calorimetric analysis in order to assess the range of the temperatures of phase transition, identified between 26 and 137 ° C as a result of the crystalline phase melting.

5 In addition, the glass adhesion properties were determined as follows. A 0.3mm thick sample was prepared through lamination process at 150 ° C on glass specimens with overlapping section of 25*10mm. The sample was subjected to a tensile test, applying a pre-load of 1N for 10s (preload speed of 1 mm / min) and then a load cell of 10 kN (also this with a test speed of 1 mm / min).

10 The test result showed a high adhesion to glass for a minimum adhesion force of 1250N for a specimen thickness of 0.3mm.

EXAMPLE 2 - COMPARATIVE

The process described in Example 1 was repeated with the only difference that no ethylene-vinylacetate copolymer was added. Thus, a polymer composition identical to
15 that described in Example 1 was prepared, but devoid of any ethylene-vinyl acetate copolymer.

The resulting composition was subjected to lap shear test in order to determine the adhesion properties on glass. The test result showed a high adhesion to glass for a minimum adhesion force of 1140N for a specimen thickness of 0.3 mm. This value
20 shows a reduction of 10% of the adhesion properties, compared to the formulation employing ethylene-vinyl acetate copolymer.

EXAMPLE 3 - COMPARATIVE

25 A polymer composition was obtained by the method of preparation described in example 1, but using, as the sole polymeric component, poly(isobutylene) having a weight-average molar mass of 60,000 g / mol. The above-mentioned polymeric component and a preserving agent, talc, carbon black and calcium oxide in similar proportions by weight to those used for examples 1 and 2 were introduced in a thermostated chamber containing two counterrotating tools set to a constant speed.

30 The analysis in differential scanning calorimetry shows a reversible endothermic transition due to the melting of a limited crystalline fraction between 36 and 120 ° C

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melting. This analysis shows that above 120 ° C the material is completely melted with a consequent drastic reduction of the mechanical properties.

CLAIMS

1. Sealant composition for insulation of moisture sensitive devices, comprising:

- 5 - at least one ethylene-octene copolymer;
 - a maleic anhydride modified polyolefin;
 - an ethylene-vinyl acetate copolymer;
 - at least one inert filler;
 - at least one moisture scavenger;
10 - at least one stabilizing or antioxidant preserving agent.

2. Composition according to the previous claim, characterized in that the weights of said ethylene-octene copolymer, maleic anhydride modified polyolefin, ethylene-vinyl acetate copolymer, inert filler, moisture scavenger and preserving agent sum up to at least 95% of the total weight of the composition.

- 15 3. Composition according to claim 1, characterized in that said maleic anhydride modified polyolefin is a polyethylene/polypropylene copolymer modified with maleic anhydride.

4. Composition according to the previous claim, characterized in that said polyethylene/polypropylene copolymer modified with maleic anhydride has a Melt
20 Flow Index higher than 1 g/10 min and a density of between 0.87 and 0.96 g/cc.

5. Composition according to claim 1, characterized in that said ethylene-octene copolymer has a melt Flow Index equal or higher than 5g/10 min.

6. Composition according to claim 5 characterized in that it further comprises a second ethylene-octene copolymer, said second ethylene-octene copolymer having a
25 melt Flow Index equal or higher than 30 g/10 min.

7. Composition according to claim 1 characterized in that said ethylene-vinyl acetate copolymer has a vinyl acetate content higher than 30% by weight and a Melt Flow Index higher than 30g/10 min.

8. Composition according to claim 1, characterized in that said at least one
30 inert filler comprises a mixture of talc and carbon black in weight proportion of between 6:1 and 8:1, more preferably between 2:1 and 4:1.

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9. Composition according to claim 1, characterized in that said at least one moisture scavenger comprises powders of one or more compounds selected among lithium oxide, calcium oxide, strontium oxide, barium oxide, magnesium oxide and aluminosilicates.

5 10. Composition according to claim 9, characterized in that said at least one moisture scavenger comprises calcium oxide and magnesium oxide.

11. Composition according to claim 1, characterized in that it comprises at least one flame retardant.

10 12. Composition according to one of the previous claims, characterized in that it comprises:

- said maleic anhydride modified polyolefin in an amount of between 5% and 20% by weight with respect to the total weight of the composition;
- said ethylene-octene copolymers in an amount of between 40% and 60% by weight with respect to the total weight of the composition;
- 15 - said ethylene-vinyl acetate copolymer in an amount of between 0.5% and 5% by weight with respect to the total weight of the composition;
- said at least one inert filler in an amount of between 1% and 30% by weight with respect to the total weight of the composition;
- said at least one moisture scavenger in an amount of between 20% and 40%
20 by weight with respect to the total weight of the composition;
- said at least one stabilizing or antioxidant preserving agent in an amount of between 0.5% and 5% by weight with respect to the total weight of the composition.

25 13. Composition according to the previous claim, characterized in that it comprises:

- said maleic anhydride modified polyolefin in an amount of between 8% and 10% by weight with respect to the total weight of the composition;
- said ethylene-octene copolymers in an amount of between 50% and 55% by weight with respect to the total weight of the composition;
- 30 - said ethylene-vinyl acetate copolymer in an amount of between 1% and 4% by weight with respect to the total weight of the composition;

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- said at least one inert filler in an amount of between 1% and 10% by weight with respect to the total weight of the composition;
 - said at least one moisture scavenger in an amount of between 25% and 35% by weight with respect to the total weight of the composition;
 - 5 - said at least one stabilizing or antioxidant preserving agent in an amount of between 1% and 3% by weight with respect to the total weight of the composition; and
 - said at least one flame retardant in an amount of between 0.5% and 3% by weight with respect to the total weight of the composition.
- 10 14. Use of a composition according to any of claims 1 to 13 as sealant in a moisture sensitive device.
- 15 15. Solar module comprising at least one among photovoltaic cells, photoelectrochemical solar cells (SSPECs) and dye sensitized solar cells (DSSCs), said module having at least a first substrate and at least one second substrate, characterized in that between said first substrate and said second substrate is positioned a composition according to any of claims 1 to 12.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2013/051860

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L23/08 H01L31/048 H01L31/18
ADD.

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)
C08L H01L C09J

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

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

EP0-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2008/115825 A1 (PATEL RAJEN M [US] ET AL) 22 May 2008 (2008-05-22) claims 1,2,10,11 paragraphs [0085], [0086]; examples A,B paragraphs [0077], [0078] page 11; table 7	1-15
A	----- WO 98/09808 A1 (BICC CABLES CORP [US]; FLENNIKEN CINDY L [US]) 12 March 1998 (1998-03-12) claims 1-3,7-10 page 13; example 1 page 3, line 35 - page 4, line 23	1-15
A	----- US 2006/201544 A1 (INOUE ISAO [JP]) 14 September 2006 (2006-09-14) claims 1-7 ----- -/--	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

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

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

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INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 2 270 077 A1 (ASAHI KASEI E MATERIALS CORP [JP]) 5 January 2011 (2011-01-05) claims 1-5,15,16 paragraphs [0044], [0045] -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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