



(11) **EP 3 546 541 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
02.10.2019 Bulletin 2019/40

(51) Int Cl.:
C09J 7/22 ^(2018.01) **B32B 13/12** ^(2006.01)

(21) Application number: **18164382.6**

(22) Date of filing: **27.03.2018**

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(71) Applicant: **SIKA TECHNOLOGY AG**
6340 Baar (CH)

(72) Inventors:
• **Gössi, Matthias**
8610 Uster (CH)
• **Mennecke, Klaas**
79807 Lottstetten (DE)

(74) Representative: **Sika Patent Attorneys**
c/o Sika Technology AG
Corp. IP Dept.
Tüffenwies 16
Postfach
8048 Zürich (CH)

(54) **A WATERPROOFING MEMBRANE WITH A FUNCTIONAL LAYER**

(57) The invention is directed to waterproofing membrane comprising a barrier layer and a functional layer, which are directly or indirectly connected over at least a part of their opposing surfaces, wherein the functional layer is composed of an at least partially cured moisture curing composition comprising at least one silane-termi-

nated polymer. The invention is also directed to a method for producing a waterproofing membrane, to a method for waterproofing a substrate, to a waterproofed substrate, and to the use of the waterproofing membrane for sealing of under and above ground structures against water penetration.

EP 3 546 541 A1

Description**Technical field**

- 5 **[0001]** The invention relates to waterproofing membranes for use in the construction industry, for example for basements, roofing and tunneling applications to protect structures against water penetration.

Background of the invention

- 10 **[0002]** Waterproofing membranes are commonly used in the construction industry for sealing bases, underground surfaces or buildings against water penetration.

- [0003]** State-of-the-art waterproofing membranes are typically multilayer systems comprising a polymer-based barrier layer as the principal layer to provide watertightness. Typical polymers used in barrier layers include thermoplastics such as plasticized polyvinylchloride (p-PVC) and thermoplastic polyolefins (TPO) or elastomers such as ethylene-propylene diene monomer (EPDM) and crosslinked chlorosulfonated polyethylene (CSPE). One of the drawbacks of polymer-based barrier layers is their poor bonding properties; they typically show low bonding strength to adhesives that are commonly used in the construction industry, such as epoxy adhesives, polyurethane adhesives, and cementitious compositions. Therefore, a contact layer, for example, a fleece backing, is typically used to provide sufficient bonding of the polymer-based barrier layer and the structure to be waterproofed.

- 20 **[0004]** In post-applied waterproofing applications, a waterproofing membrane is bonded to a surface of a structure to be waterproofed whereas in pre-applied applications, the waterproofing membrane is laid before the structure to be waterproofed is built. In the first case, the membrane is bonded via its contact layer to the surface of the structure by using an adhesive or a sealing tape. In the latter case, the waterproofing membrane is placed with its waterproofing layer against an underlying structure or formwork and fresh concrete is cast against the surface of the contact layer, thereby fully and permanently bonding the membrane to the surface of the hardening concrete. A layer of adhesive can be used between the waterproofing layer and the contact layer to improve bonding to the fresh concrete cast. The adhesive should preferably enable penetration of the casted concrete into the contact layer in order to ensure good bonding between waterproofing membrane and the surface of the waterproofed structure.

- 25 **[0005]** One of the main challenges related to the multilayer waterproofing membranes is to ensure watertightness after infiltration in case of leak in the barrier layer. Watertightness after infiltration means in general that the sealing construction should be able to prevent the infiltrated water from penetrating to the space between the membrane and the waterproofed surface. A leak in the barrier layer can be a result of inward growing tree roots, material failure or tensile or shear forces directed to the membrane. If the watertightness after infiltration is lost, water is able to flow laterally underneath the membrane and to invade the interior of the building structure. In such cases the exact location of the leak in the barrier layer is also difficult to detect.

- 30 **[0006]** US 8793862 B2 describes a waterproofing membrane comprising a barrier layer, a composite layer arranged on one side of the barrier layer and a network of sealant between the barrier layer and the composite layer. The network of sealant is said to limit the size of area affected by penetrating water in case of water leakage through the barrier layer. In waterproofing applications the membrane is applied on a subsurface in such a way that the barrier layer is directed against a concrete base and the composite layer is facing the concrete casted against the membrane. During the hardening process, the composite layer is penetrated by the liquid concrete forming a good bond with the hardened concrete.

- 35 **[0007]** US2015/0231863 A1 discloses a waterproofing membrane including a barrier layer and a functional layer including a thermoplastic polymer that changes consistency under the influence of highly alkaline media and an adhesive. Once the functional layer gets into contact with liquid concrete, the thermoplastic polymer dissolves and allows the adhesive to bond to the cast concrete. The functional layer may additionally comprise other thermoplastic polymers, fillers or concrete constituents. The construction of the functional layer is said to enable working with membranes in adverse weather conditions without diminishing the adhesive capacity of the membrane.

- 40 **[0008]** One of the disadvantages of the State-of-the-Art multilayer waterproofing membranes is related to the use of non-woven backings as contact layer to provide sufficient bonding between the membrane and the substrate to be waterproofed. In waterproofing and roofing applications the adjacent membrane sheets have to be homogeneously joined to each other in a reliable way to ensure watertightness of the sealing construction. Membranes having a non-woven backing cannot typically be joined by heat welding but instead the edges of the membranes have to be bonded together either by using an adhesive or with a sealing tape adhered on top of the seam and/or under the seam. The use of an adhesive or a sealing tape to join adjacent membrane sheets complicates the installation process and increases application costs.

- 55 **[0009]** There is thus a need for a novel type of waterproofing membrane, which is suitable for use in pre-applied waterproofing applications and which provides high bonding strength with casted concrete after hardening without the

use of a non-woven backing.

Summary of the invention

[0010] The object of the present invention is to provide a waterproofing membrane, which can be used for sealing of bases, underground surfaces or buildings against water penetration. In particular it is the objective of the present invention to provide a waterproofing membrane, which forms a permanent bond with a layer of cementitious composition after hardening without the use of a fiber-based contact layer.

[0011] The subject of the present invention is a sealing device as defined in claim 1.

[0012] It was surprisingly found that the fiber-based contact layer typically used in prior art waterproofing membranes can be replaced with a functional layer composed of an at least partially cured moisture curing composition comprising at least one silane-terminated polymer.

[0013] One of the advantages of the present invention is that unlike a fiber-based contact layer, the functional layer of the present invention is relatively easy to clean by a simple washing step. This is a significant advantage since the waterproofing membranes are typically not stored in the form of rolls on the construction site but instead the membranes are spread out on the surface to be waterproofed with the functional layer facing upwards long before the casting of the concrete layer. The time period between the casting of the concrete layer and installation of the waterproofing membrane can be relatively long and during that time the functional layer is susceptible to environmental conditions, such as effects of heat, UV-exposure, rain, and in particular foot traffic across the membrane surface.

[0014] Since the waterproofing membranes are usually not provided with additional protective layers, which would protect the functional layer from dirt accumulation, the outer surface of the membrane has to be cleaned by washing before the casting of the concrete layer to ensure proper bonding between the casted concrete and the functional layer. Washing of fiber-based contact layers is per se a complicated process due to the porous structure of the contact layer. The sufficiency of the cleaning treatment is also difficult to verify since the dirt particles are typically absorbed deep inside the fiber-based contact layer.

[0015] Other aspects of the present invention are presented in other independent claims. Preferred aspects of the invention are presented in the dependent claims.

Brief description of the Drawings

[0016]

Fig. 1 shows a cross-section of a waterproofing membrane (1) comprising a barrier layer (2) and a functional layer (3) covering the first major surface of the barrier layer (2).

Fig. 2 shows a cross-section of a waterproofing membrane (1) comprising a barrier layer (2), a functional layer (3), and a connecting layer (4) arranged between the barrier layer (2) and the functional layer (3).

Fig. 3 shows a cross-section of a waterproofed construction comprising a substrate (5) and a layer of concrete (6) and a waterproofing membrane (1) arranged between the outer surface of the substrate (5) and the layer of concrete (6) such that the first surface of the barrier layer (2) is directed against the outer surface of the substrate and the second surface of the functional layer is bonded to the layer of concrete (6).

Detailed description of the invention

[0017] The subject of the present invention is a waterproofing membrane comprising a waterproofing membrane comprising a barrier layer having first and second major surfaces and a functional layer having first and second major surfaces, wherein the functional layer and the barrier layer are directly or indirectly connected over at least a part of their opposing major surfaces and wherein the functional layer is composed of an at least partially cured moisture curing composition comprising:

- a) At least one silane-terminated polymer and
- b) Optionally at least one monomeric silane crosslinker.

[0018] Substance names beginning with "poly" designate substances which formally contain, per molecule, two or more of the functional groups occurring in their names. For instance, a polyol refers to a compound having at least two hydroxyl groups. A polyether refers to a compound having at least two ether groups.

[0019] The term "polymer" designates a collective of chemically uniform macromolecules produced by a polyreaction

(polymerization, polyaddition, polycondensation) where the macromolecules differ with respect to their degree of polymerization, molecular weight and chain length. The term also comprises derivatives of said collective of macromolecules resulting from polyreactions, that is, compounds which are obtained by reactions such as, for example, additions or substitutions, of functional groups in predetermined macromolecules and which may be chemically uniform or chemically nonuniform.

[0020] The term "polyurethane polymer" designates polymers prepared by so called diisocyanate polyaddition process. This also includes those polymers which are virtually free or entirely free from urethane groups. Examples of polyurethane polymers are polyether-polyurethanes, polyester-polyurethanes, polyether-polyureas, polyureas, polyester-polyureas, polyisocyanurates, and polycarbodiimides.

[0021] The terms "silane" and "organosilane" respectively identify compounds which in the first instance have at least one, customarily two or three, hydrolyzable groups bonded directly to the silicon atom via Si-O- bonds, more particularly alkoxy groups or acyloxy groups, and in the second instance have at least one organic radical bonded directly to the silicon atom via an Si-C bond. Silanes with alkoxy or acyloxy groups are also known to the person skilled in the art as organoalkoxysilanes and organoacyloxysilanes, respectively. Tetraalkoxysilanes, consequently, are not organosilanes under this definition.

[0022] Correspondingly, the term "silane group" designates the silicon-containing group bonded to the organic carbon radical via the Si-C bond. The silanes, and their silane groups, have the property of undergoing hydrolysis on contact with moisture. In so doing, they form organosilanols, these being organosilicon compounds containing one or more silanol groups (Si-OH groups) and, by subsequent condensation reactions, organosiloxanes, these being organosilicon compounds containing one or more siloxane groups (Si-O-Si groups).

[0023] The term "silane-functional" designates compounds which have silane groups. "Silane-functional polymers" accordingly, are polymers which have at least one silane group. The term "silane-terminated polymer" designates polymers having silane-groups at their chain ends.

[0024] Silane designations with functional groups as prefixes such as "aminosilanes" or "mercaptosilanes", for example, identify silanes which carry the stated functional group on the organic radical as a substituent.

[0025] The terms "organotitanate", "organozirconate", "organostannates", and "organoaluminate" in the present document identify compounds which have at least one organic ligand bonding via an oxygen atom to the titanium, zirconium, tin, and aluminum atom, respectively.

[0026] In this document, an amine or an isocyanate is called "aliphatic" when its amine group or its isocyanate group, respectively, is directly bound to an aliphatic, cycloaliphatic or arylaliphatic moiety. The corresponding functional group is therefore called an aliphatic amine or an aliphatic isocyanate group, respectively.

[0027] In this document, an amine or an isocyanate is called "aromatic" when its amine group or its isocyanate group, respectively, is directly bound to an aromatic moiety. The corresponding functional group is therefore called an aromatic amine or an aromatic isocyanate group, respectively.

[0028] The term "primary amine group" designates an NH_2 -group bound to an organic moiety, and the term "secondary amine group" designates a NH-group bound to two organic moieties which together may be part of a ring.

[0029] The term "(meth)acrylic" designates methacrylic or acrylic. Accordingly, (meth)acryloyl designates methacryloyl or acryloyl. A (meth)acryloyl group is also known as (meth)acryl group. A (meth)acrylic compound can have one or more (meth)acryl groups, such as mono- di-, tri- etc. functional (meth)acrylic compounds.

[0030] The term "molecular weight" designates the molar mass (g/mol) of a molecule or a part of a molecule, also referred to as "moiety". The term "average molecular weight" designates the number average molecular weight (M_n) of an oligomeric or polymeric mixture of molecules or moieties. The number average molecular weight can be determined by gel permeation chromatography (GPC) with a polystyrene standard.

[0031] The term "glass transition temperature" (T_g) designates the temperature above which temperature a polymer component becomes soft and pliable, and below which it becomes hard and glassy. The glass transition temperature is preferably determined differential scanning calorimetry method (DSC) according to ISO 11357 standard using a heating rate of 2 °C/min. The measurements can be performed with a Mettler Toledo DSC 3+ device and the T_g values can be determined from the measured DSC-curve with the help of the DSC-software.

[0032] The term "softening point" designates a temperature at which compound softens in a rubber-like state, or a temperature at which the crystalline portion within the compound melts. The softening point can be measured by a ring and ball method according to DIN EN 1238.

[0033] The "amount or content of at least one component X" in a composition, for example "the amount of the at least one thermoplastic polymer P" refers to the sum of the individual amounts of all thermoplastic polymers P contained in the composition. For example, in case the composition comprises 20 wt.-% of at least one thermoplastic polymer P, the sum of the amounts of all thermoplastic polymers P contained in the composition equals 20 wt.-%.

[0034] The term "room temperature" designates a temperature of 23°C.

[0035] A dashed line in the chemical formulas of this document represents the bonding between a moiety and the corresponding rest of the molecule.

[0036] The barrier layer is preferably a planar element having first and second major surfaces, i.e. top and bottom surfaces, defined by peripheral edges. The term "planar element" designates in the present document sheet-like elements having a length and width at least 50 times, preferably at least 100 times, more preferably at least 500 times, greater than the thickness of the element.

[0037] The functional layer is composed of an at least partially cured moisture curing composition. The term "curing composition" or "curable composition" designates in the present document compositions, which can be cured by initiation of the curing reactions. The term "curing reaction" designates in the present document chemical reactions comprising forming bonds resulting, for example, in chain extension and/or crosslinking of polymer chains. The term "cured" as used in connection with a curing composition, for example "at least partially cured moisture curing composition", is understood to mean that at least a portion of the polymerizable and/or crosslinkable components that form the moisture curing composition is cured. It may be preferable that the functional layer is composed of a moisture curing composition having a curing degree of reactive groups, in particular curing degree of silane groups of at least 15%, preferably at least 35%, more preferably at least 55%, even more preferable at least 65%, most preferably at least 75%. The term "curing degree of silane groups" designates the number of silane groups that have undergone a curing reaction relative to the number of silane groups that were originally unreacted before initiation of the curing reactions. Furthermore, it may be preferable that the functional layer is composed of a moisture curing composition having a curing degree of reactive groups, in particular curing degree of silane groups of at least 85%, more preferably at least 95%, even more preferably at least 97.5%, most preferable at least 99%.

[0038] It may be preferable that the functional layer is composed of a moisture curing composition that is essentially completely cured. The term "essentially completely cured" is understood to mean that the composition has a curing degree of all reactive groups, in particular of silane, epoxy, and amine groups, of at least of at least 85%, more preferably at least 95%, even more preferably at least 97.5%, most preferable at least 99%.

[0039] According to one or more embodiments, the functional layer is composed of a continuous layer of at least partially cured moisture curing composition. The term "continuous layer" designates in the present document layers consisting of one single area of the respective material. In contrast, a "discontinuous layer" is considered to consist of more than one areas of the respective material, which areas are not connected with each other to form one single continuous layer of the material.

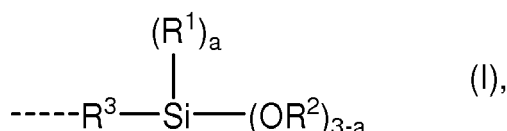
[0040] The functional layer and the barrier layer are at directly or indirectly connected over at least a part of their opposing major surfaces. It may, however, be preferable that substantially the entire area of the first major surface of the functional layer is directly or indirectly connected to the second major surface of the waterproofing layer. It may furthermore be preferable that the functional layer and the waterproofing layer have substantially the same width and length.

[0041] According to one or more embodiments, the functional layer and the barrier layer are directly connected to each other over at least a part of their opposing major surfaces. The expression "directly connected" is understood to mean in the context of the present invention that no further layer or substance is present between the layers, and that the opposing surfaces of the two layers are directly bonded to each other or adhere to each other. At the transition area between the two layers, the materials forming the layers can also be present mixed with each other. According to one or more embodiments, substantially the entire first major surface of the functional layer is directly connected to the second major surface of the barrier layer. In these embodiments, it may for example be preferable that at least 90%, more preferably at least 95%, of the first major surface of the functional layer is directly connected to the second major surface of the barrier layer.

[0042] The moisture curing composition may be a single-component moisture curing composition or a multiple-component moisture curing composition, in particular a two-component moisture curing composition. In case of a multiple-component composition, the at least partially cured moisture curing composition is obtained by mixing the components of the multiple-component moisture curing composition with each other and allowing the thus obtained mixture to cure.

[0043] The term "single-component composition" or "single-part composition" designates in the present document storage-stable compositions, in which the constituents of the composition are provided in a one component. Single-component compositions can be provided packaged in one package whereas in two-component or multi-component compositions the components are provided packaged in physically separated compartments or in separate packages in order to ensure storage-stability. The terms "storage stability" and "shelf life stability" refer to the ability of a composition to be stored at room temperature in a suitable container under exclusion of moisture for a certain time interval, in particular several months, without undergoing significant changes in application or end-use properties.

[0044] Preferably, the at least one silane-terminated polymer has at least one terminal group of formula (I):



wherein

R¹ is an alkyl- group having 1 to 8 C atoms,

R² is an acyl or alkyl group having 1 to 5 C atoms,

R³ is a linear or branched, or cyclic, alkylene group having 1 to 12 C atoms, optionally with aromatic moieties, and optionally with 1 or more heteroatoms, and

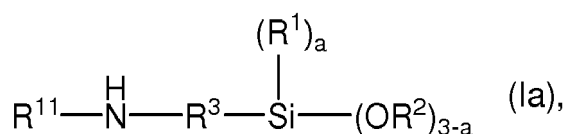
a is 0 or 1 or 2, preferably 0.

[0045] Within a silane group of the formula (I), R¹ and R², each independently of one another, are the radicals as described. Thus, for example, possible compounds of the formula (I) include those which represent the ethoxy-dimethoxy-alkylsilanes (R² = methyl, R² = methyl, R² = ethyl).

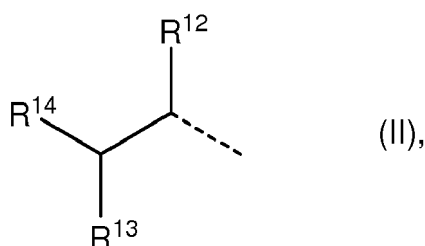
[0046] Preferably, the silane-terminated polymer is a silane-terminated polyurethane polymer, more preferably a silane-terminated polyurethane polymer that is entirely free of isocyanate groups.

[0047] According to one or more embodiments, the at least one silane-terminated polymer is a silane-terminated polyurethane polymer P1, which is obtainable by the reaction of a silane having at least one group that is reactive toward isocyanate groups, with a polyurethane polymer which contains terminal isocyanate groups. This reaction is carried out preferably in a stoichiometric ratio of the groups that are reactive toward isocyanate groups to the isocyanate groups of 1:1, or with a slight excess of groups that are reactive toward isocyanate groups, meaning that the resulting silane-terminated polyurethane polymer is preferably entirely free of isocyanate groups.

[0048] Suitable silanes which have at least one group that is reactive toward isocyanate groups include, for example, mercaptosilanes, aminosilanes, and hydroxysilanes, in particular aminosilanes and hydroxysilanes. Particularly suitable aminosilanes include aminosilanes of the formula (Ia):



wherein the radicals R¹, R², R³, and a have the already described meanings and R¹¹ is a hydrogen atom or is a linear or branched hydrocarbon radical having 1 to 20 C atoms that optionally contains cyclic moieties, or is a radical of the formula (II):



wherein the radicals R¹² and R¹³, independently of one another, are a hydrogen atom or a radical from the group encompassing -R¹⁵, -CN, and -COOR¹⁵, radical R¹⁴ is a hydrogen atom or is a radical from the group encompassing -CH₂-COOR¹⁵, -COOR¹⁵, CONHR¹⁵, -CON(R¹⁵)₂, -CN, -NO₂, -PO(OR¹⁵)₂, -SO₂R¹⁵, and -SO₂OR¹⁵, and the radical R¹⁵ is a hydrocarbon radical having 1 to 20 C atoms that optionally comprises at least one heteroatom.

[0049] Examples of preferred aminosilanes are primary aminosilanes such as 3-aminopropyltriethoxysilane, 3-aminopropyl-diethoxymethylsilane; secondary aminosilanes such as N-butyl-3-aminopropyltriethoxysilane, N-phenyl-3-aminopropyltriethoxysilane; the products of the Michael-like addition of primary aminosilanes such as 3-aminopropyltriethoxysilane or 3-aminopropyl-diethoxymethylsilane onto Michael acceptors such as acrylonitrile, (meth)acrylic esters, (meth)acrylamides, maleic diesters and fumaric diesters, citraconic diesters and itaconic diesters, examples being dimethyl and diethyl N-(3-triethoxysilylpropyl)aminosuccinate; and also analogs of the stated aminosilanes having methoxy

or isopropoxy groups instead of the preferred ethoxy groups on the silicon. Particularly suitable aminosilanes are secondary aminosilanes, more particularly aminosilanes in which R^4 in formula (II) is different from H. Preferred are the Michael-like adducts, more particularly diethyl N-(3-triethoxysilylpropyl)aminosuccinate.

[0050] The term "Michael acceptor" designates in the present document compounds which on the basis of the double bonds they contain, activated by electron acceptor radicals, are capable of entering into nucleophilic addition reactions with primary amino groups (NH_2 groups) in a manner analogous to Michael addition (hetero-Michael addition).

[0051] Particularly suitable hydroxysilanes include the ones disclosed, for example, in WO 2014/187865 A1, WO 2015/014725 A1, WO 2015/014726 A1, WO 2016/083310 A1, WO 2016/083311 A1, WO 2016/083312 A1, and WO 2016/083309 A1.

[0052] Examples of suitable polyurethane polymers containing isocyanate groups for the preparation of a silane-terminated polyurethane polymer include polymers which are obtainable by the reaction of at least one polyol with at least one polyisocyanate, more particularly a diisocyanate. This reaction may take place by the polyol and the polyisocyanate being reacted by customary methods, as for example at temperatures of 50°C to 100°C, optionally with accompanying use of suitable catalysts, the polyisocyanate being metered such that its isocyanate groups are present in a stoichiometric excess in relation to the hydroxyl groups of the polyol.

[0053] More particularly the excess of polyisocyanate is preferably selected such that in the resulting polyurethane polymer, after the reaction of all hydroxyl groups of the polyol, the remaining free isocyanate group content is from 0.1 to 5 wt.-%, preferably 0.1 to 2.5 wt.-%, more preferably 0.2 to 1 wt.-%, based on the overall polymer.

[0054] The polyurethane polymer may optionally be prepared with accompanying use of plasticizers, in which case the plasticizers used contain no groups that are reactive toward isocyanates.

[0055] Preferred polyurethane polymers with the stated amount of free isocyanate groups are those obtained from the reaction of diisocyanates with high molecular mass diols in an NCO:OH ratio of 1.5:1 to 2:1.

[0056] Suitable polyols for preparing the polyurethane polymer are, in particular, polyether polyols, polyester polyols, and polycarbonate polyols, and also mixtures of these polyols.

[0057] Especially suitable polyether polyols, also called polyoxyalkylene polyols or oligoetherols, are those which are polymerization products of ethylene oxide, 1,2-propylene oxide, 1,2- or 2,3-butylene oxide, oxetane, tetrahydrofuran, or mixtures thereof, optionally polymerized with the aid of a starter molecule having two or more active hydrogen atoms, such as water, ammonia, for example, or compounds having two or more OH or NH groups such as, for example, 1,2-ethanediol, 1,2- and 1,3-propanediol, neopentyl glycol, diethylene glycol, triethylene glycol, the isomeric dipropylene glycols and tripropylene glycols, the isomeric butanediols, pentanediols, hexanediols, heptanediols, octanediols, nonanediols, decanediols, undecanediols, 1,3- and 1,4-cyclohexanedimethanol, bisphenol A, hydrogenated bisphenol A, 1,1,1-trimethylolethane, 1,1,1-trimethylolpropane, glycerol, aniline, and mixtures of the stated compounds. Use may be made both of polyoxyalkylene polyols which have a low degree of unsaturation (measured by ASTM D-2849-69 and expressed in milliequivalents of unsaturation per gram of polyol (meq/g)), prepared for example by means of double metal cyanide complex catalysts (DMC catalysts), and of polyoxyalkylene polyols having a higher degree of unsaturation, prepared for example by means of anionic catalysts such as NaOH, KOH, CsOH, or alkali metal alkoxides.

[0058] Particularly suitable are polyoxyethylene polyols and polyoxypropylene polyols, more particularly polyoxyethylene diols, polyoxypropylene diols, polyoxyethylene triols, and polyoxypropylene triols.

[0059] Especially suitable are polyoxyalkylene diols or polyoxyalkylene triols having a degree of unsaturation of less than 0.02 meq/g and having an average molecular weight in the range from 1,000 to 30,000 g/mol, and also polyoxyethylene diols, polyoxyethylene triols, polyoxypropylene diols, and polyoxypropylene triols having an average molecular weight of 400 to 20,000 g/mol. Likewise particularly suitable are so-called ethylene oxide-terminated ("EO-endcapped", ethylene oxide-endcapped) polyoxypropylene polyols. The latter are special polyoxypropylene-polyoxyethylene polyols which are obtained, for example, by subjecting pure polyoxypropylene polyols, more particularly polyoxypropylene diols and triols, to further alkoxylation with ethylene oxide after the end of the polypropoxylation reaction, and which therefore have primary hydroxyl groups. Preferred in this case are polyoxypropylene-polyoxyethylene diols and polyoxypropylene-polyoxyethylene triols.

[0060] Additionally suitable are hydroxyl group terminated polybutadiene polyols, examples being those prepared by polymerization of 1,3-butadiene and allyl alcohol or by oxidation of polybutadiene, and their hydrogenation products.

[0061] Additionally suitable are styrene-acrylonitrile grafted polyether polyols, of the kind available commercially, for example, under the trade name Lupranol® from BASF SE, Germany.

[0062] Especially suitable as polyester polyols are polyesters which carry at least two hydroxyl groups and are prepared by known processes, particularly by the polycondensation of hydroxycarboxylic acids or the polycondensation of aliphatic and/or aromatic polycarboxylic acids with dihydric or polyhydric alcohols.

[0063] Especially suitable polyester polyols are those prepared from di- to trihydric alcohols such as, for example, 1,2-ethanediol, diethylene glycol, 1,2-propanediol, dipropylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, glycerol, 1,1,1-trimethylolpropane, or mixtures of the aforesaid alcohols, with organic dicarboxylic acids or their anhydrides or esters, such as, for example, succinic acid, glutaric acid, adipic acid, trimethyladipic acid, suberic

acid, azelaic acid, sebacic acid, dodecanedicarboxylic acid, maleic acid, fumaric acid, dimer fatty acid, phthalic acid, phthalic anhydride, isophthalic acid, terephthalic acid, dimethyl terephthalate, hexahydrophthalic acid, trimellitic acid, and trimellitic anhydride, or mixtures of the aforesaid acids, and also polyester polyols of lactones such as ϵ -caprolactone, for example.

[0064] Particularly suitable are polyester diols, especially those prepared from adipic acid, azelaic acid, sebacic acid, dodecanedicarboxylic acid, dimer fatty acid, phthalic acid, isophthalic acid, and terephthalic acid as dicarboxylic acid, or from lactones such as ϵ -caprolactone, for example, and from ethylene glycol, diethylene glycol, neopentyl glycol, 1,4-butanediol, 1,6-hexanediol, dimer fatty acid diol, and 1,4-cyclohexanedimethanol as dihydric alcohol.

[0065] Especially suitable polycarbonate polyols are those obtainable by reaction, for example, of the abovementioned alcohols, used for synthesis of the polyester polyols, with dialkyl carbonates such as dimethyl carbonate, diaryl carbonates such as diphenyl carbonate, or phosgene. Particularly suitable are polycarbonate diols, especially amorphous polycarbonate diols.

[0066] Other suitable polyols are poly(meth)acrylate polyols.

[0067] Likewise suitable, moreover, are polyhydrocarbon polyols, also called oligohydrocarbonols, examples being polyhydroxy-functional ethylene-propylene, ethylene-butylene or ethylene-propylene-diene copolymers, as produced for example by Kraton Polymers, USA, or polyhydroxy-functional copolymers of dienes such as 1,3-butadiene or diene mixtures and vinyl monomers such as styrene, acrylonitrile or isobutylene, or polyhydroxy-functional polybutadiene polyols, examples being those which are prepared by copolymerization of 1,3-butadiene and allyl alcohol and which may also have been hydrogenated.

[0068] Additionally suitable are polyhydroxy-functional acrylonitrile/butadiene copolymers of the kind preparable, for example, from epoxides or amino alcohols and carboxyl-terminated acrylonitrile/butadiene copolymers, which are available commercially under the name Hypro® (formerly Hycar® CTBN from Emerald Performance Materials, LLC, USA).

[0069] These stated polyols preferably have a molecular weight of 250 to 30,000 g/mol, more particularly of 1,000 to 30,000 g/mol, and an average OH functionality in the range from 1.6 to 3.

[0070] Particularly suitable polyols are polyester polyols and polyether polyols, more particularly polyether polyols, such as polyoxyethylene polyol, polyoxypropylene polyol, and polyoxypropylene-polyoxyethylene polyol, preferably polyoxyethylene diol, polyoxypropylene diol, polyoxyethylene triol, polyoxypropylene triol, polyoxypropylene-polyoxyethylene diol, and polyoxypropylene-polyoxyethylene triol.

[0071] Further to these stated polyols it is possible as well to use small amounts of low molecular weight dihydric or polyhydric alcohols such as, for example, 1,2-ethanediol, 1,2- and 1,3-propanediol, neopentyl glycol, diethylene glycol, triethylene glycol, the isomeric dipropylene glycols and tripropylene glycols, the isomeric butanediols, pentanediols, hexanediols, heptanediols, octanediols, nonanediols, decanediols, undecanediols, 1,3- and 1,4-cyclohexanedimethanol, hydrogenated bisphenol A, dimeric fatty alcohols, 1,1,1-trimethylolethane, 1,1,1-trimethylolpropane, glycerol, pentaerythritol, sugar alcohols such as xylitol, sorbitol or mannitol, sugars such as sucrose, other higher alcohols, low molecular weight alkoxylation products of the aforesaid dihydric and polyhydric alcohols, and also mixtures of the aforesaid alcohols, when preparing the polyurethane polymer having terminal isocyanate groups.

[0072] As polyisocyanates for the preparation of the polyurethane polymer it is possible to use commercially customary aliphatic, cycloaliphatic or aromatic polyisocyanates, more particularly diisocyanates. Suitable diisocyanates by way of example are those whose isocyanate groups are bonded in each case to one aliphatic, cycloaliphatic or arylaliphatic C atom, also called "aliphatic diisocyanates", such as 1,6-hexamethylene diisocyanate (HDI), 2-methylpentamethylene 1,5-diisocyanate, 2,2,4- and 2,4,4-trimethyl-1,6-hexamethylene diisocyanate (TMDI), 1,12-dodecamethylene diisocyanate, lysine diisocyanate and lysine ester diisocyanate, cyclohexane 1,3-diisocyanate, cyclohexane 1,4-diisocyanate, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (= isophorone diisocyanate or IPDI), perhydro-2,4'-diphenylmethane diisocyanate and perhydro-4,4'-diphenylmethane diisocyanate, 1,4-diisocyanato-2,2,6-trimethylcyclohexane (TMCDI), 1,3- and 1,4-bis(isocyanatomethyl)cyclohexane, m- and p-xylylene diisocyanate (m- and p-XDI), m- and p-tetramethyl-1,3-xylylene diisocyanate, m- and p-tetramethyl-1,4-xylylene diisocyanate, bis(1-isocyanato-1-methylethyl)naphthalene; and also diisocyanates having isocyanate groups bonded in each case to one aromatic C atom, also called "aromatic diisocyanates", such as 2,4- and 2,6-tolylene diisocyanate (TDI), 4,4'-, 2,4'-, and 2,2'-diphenylmethane diisocyanate (MDI), 1,3- and 1,4-phenylene diisocyanate, 2,3,5,6-tetramethyl-1,4-diisocyanatobenzene, naphthalene 1,5-diisocyanate (NDI), 3,3'-dimethyl-4,4'-diisocyanatodiphenyl (TODI); oligomers and polymers of the aforementioned isocyanates, and also any desired mixtures of the aforementioned isocyanates.

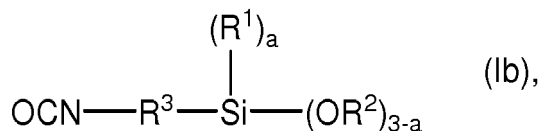
[0073] Suitable methoxysilane-functional polymers are available commercially, for example, under the trade name Polymer ST50 from Hanse Chemie AG, Germany, and also under the trade name Desmoseal® from Covestro AG, Germany.

[0074] Preferably, the silane-terminated polymer **P1** is an ethoxysilane-terminated polyurethane polymer.

[0075] According to one or more preferred embodiments, the at least one silane-terminated polymer is a silane-terminated polyurethane polymer **P2**, which is obtainable through the reaction of isocyanatosilane with a polymer which has functional end groups that are reactive toward isocyanates, these end groups being more particularly hydroxyl

groups, mercapto groups and/or amino groups. This reaction takes place in a stoichiometric ratio of the isocyanate groups to the functional end groups that are reactive toward isocyanate groups of 1:1, or with a slight excess of the functional end groups that are reactive toward isocyanate groups, at temperatures, for example, of 20°C to 100°C, optionally with accompanying use of catalysts.

[0076] Suitable isocyanatosilanes include compounds of the formula (Ib):



wherein R¹, R², R³ have the already mentioned meanings. Examples of suitable isocyanatosilanes of the formula (Ib) are 3-isocyanatopropyltriethoxysilane, 3-isocyanatopropyldiethoxymethylsilane, and their analogs with methoxy or isopropoxy groups in place of the ethoxy groups in the silica.

[0077] The polymer preferably has hydroxyl groups as functional end groups, which are reactive toward isocyanate groups of isocyanatosilane. Suitable polymers having hydroxyl groups are, on the one hand, high molecular weight polyoxyalkylene polyols already identified, preferably polyoxypropylene diols having a degree of unsaturation of less than 0.02 meq/g and having an average molecular weight in the range from 4,000 to 30,000 g/mol, more particularly those having an average molecular weight in the range from 8,000 to 30,000 g/mol.

[0078] Also suitable on the other hand are polyurethane polymers having hydroxyl groups, especially terminated with hydroxyl groups, for reaction with isocyanatosilanes of the formula (Ib). Polyurethane polymers of this kind are obtainable through the reaction of at least one polyisocyanate with at least one polyol. This reaction may be accomplished by bringing the polyol and the polyisocyanate to reaction by customary processes, at temperatures of 50°C to 100°C, for example, optionally with accompanying use of suitable catalysts, the polyol being metered such that its hydroxyl groups are in a stoichiometric excess in relation to the isocyanate groups of the polyisocyanate. Preferred is a ratio of hydroxyl groups to isocyanate groups of 1.3:1 to 4:1, more particularly of 1.8:1 to 3:1. The polyurethane polymer may optionally be prepared with accompanying use of plasticizers, in which case the plasticizers used contain no groups reactive toward isocyanates. Suitable for this reaction are the same polyols and polyisocyanates already referenced as being suitable for the preparation of a polyurethane polymer containing isocyanate groups that is used for preparing a silane-terminated polyurethane polymer **P1**.

[0079] Suitable methoxysilane-terminated polymers are commercially available, for example, under the trade names SPUR+® 1010LM, 1015LM, and 1050MM from Momentive Performance Materials Inc., USA, and also under the trade names Geniosil® STP-E15, STP-10, and STP-E35 from Wacker Chemie AG, Germany, and also under the trade name Incorez STP from Sika Incorez, UK. Preferably, the silane-terminated polymer **P2** is an ethoxysilane-terminated polyurethane polymer.

[0080] According to one or more embodiments, the silane-terminated polymer is a silane-terminated polymer **P3**, which is obtainable by a hydrosilylation reaction of polymers, having terminal double bonds, examples being poly(meth)acrylate polymers or polyether polymers, more particularly of allyl-terminated polyoxyalkylene polymers, as described for example in US 3,971,751 and US 6,207,766.

[0081] Suitable methoxysilane-terminated polymers are commercially available, for example, under the trade names MS-Polymer® S203(H), S303(H), S227, S810, MA903, and S943, Silyl® SAX220, SAX350, SAX400, and SAX725, Silyl® SAT350, and SAT400, and also XMAP® SA100S, and SA310S from Kaneka Corp., Japan, and also under the trade names Excestar® S2410, S2420, S3430, S3630, W2450, and MSX931 from Asahi Glass Co, Ltd., Japan. Preferably, the silane-terminated polymer **P3** is an ethoxysilane-terminated polymer.

[0082] It is also possible to use as the at least one silane-terminated polymers other silane-terminated polymers that are commercially available, for example, under the trade name Tegopac® from Evonik Industries, Germany, more particularly Tegopac® Seal 100, Tegopac® Bond 150, Tegopac® Bond 250.

[0083] Preferably, the at least one silane-terminated polymer is free of methoxysilane-groups, i.e. the composition preferably comprises no constituents which give off methanol upon curing in the presence of water.

[0084] According to one or more embodiments, the at least one silane-terminated polymer is present in the moisture curing composition in an amount of at least 5 wt.-%, preferably at least 10 wt.-%, more preferably at least 15 wt.-%, most preferably at least 20 wt.-%, based on the total weight of the moisture curing composition. According to one or more further embodiments, the at least one silane-terminated polymer is present in the moisture curing composition in an amount of 5 - 85 wt.-%, more preferably 10 - 75 wt.-%, even more preferably 15 - 65 wt.-%, most preferably 20 - 55 wt.-%, based on the total weight of the moisture curing composition.

[0085] According to one or more embodiments, the moisture curing composition further comprises:

b) At least one silane crosslinker.

[0086] Suitable silane crosslinkers include monomeric and oligomeric silane compounds containing one or more, preferably two or more functional residues. Particularly suitable silane crosslinkers include, for example, aminosilanes, epoxysilanes, mercaptosilanes, (meth)acrylosilanes, vinylsilanes, urea silanes, and anhydridosilanes or adducts of the aforesaid silanes with primary aminosilanes. According to one or more embodiments, the moisture curing composition comprises at least one silane crosslinker selected from the group consisting of aminosilanes, epoxysilanes, mercaptosilanes, (meth)acrylosilanes, and vinyl silanes. The presence of the silane crosslinkers has been found to improve the mechanical properties of the functional layer.

[0087] Particularly suitable silane crosslinker include vinyl trialkoxysilanes, 3-aminopropyl-dialkoxyalkylsilanes, 3-aminopropyl-trialkoxysilanes, N-(2-aminoethyl)-3-aminopropyl-dialkoxyalkylsilanes, N-(2-aminoethyl)-3-aminopropyl-trialkoxysilanes, 3-glycidoxypolytrialkoxysilanes and 3-mercaptopropyl-trialkoxysilanes. According to one or more embodiments, the at least silane crosslinker is selected from the group consisting of vinyl trimethoxysilane, vinyl triethoxysilane, 3-aminopropyl-trimethoxysilane, 3-aminopropyl-triethoxysilane, N-(2-aminoethyl)-3-aminopropyl-dimethoxymethylsilane, N-(2-aminoethyl)-3-aminopropyl-trimethoxysilane, N-(2-aminoethyl)-3-aminopropyl-triethoxysilane, 3-glycidoxypolytrimethoxysilane, 3-glycidoxypolytriethoxysilane, 3-mercaptopropyl-trimethoxysilane and 3-mercaptopropyl-triethoxysilane.

[0088] The amount of silane crosslinkers in the moisture curing composition is not particularly restricted. According to one or more embodiments, the at least one silane crosslinker is present in the moisture curing composition in an amount of 0.5 - 10.0 wt.-%, more preferably 1.0 - 7.5 wt.-%, most preferably 1.5 - 5.0 wt.-%, based on the total weight of the moisture curing composition.

[0089] According to one or more embodiments, the moisture curing composition further comprises:

c) At least one filler, preferably at least one inert mineral filler.

[0090] The term "inert mineral filler" designates in the present document mineral fillers, which, unlike mineral binders are not reactive with water, i.e. do not undergo a hydration reaction in the presence of water. The presence of inert mineral fillers in the moisture curing composition has been found out to improve the concrete adhesion strength of the functional layer. The term "concrete adhesion strength" designates in the present document the adhesive bond strength between a substrate and a surface of a concrete specimen, which has been casted on the surface of the substrate and allowed to harden. The concrete adhesion strength of a waterproofing membrane can be measured as average peel force required to separate the membrane from the surface of a cured concrete specimen.

[0091] Particularly suitable inert mineral fillers include, for example, sand, granite, calcium carbonate, calcium kaolins, diatomaceous earth, pumice, mica, talc, dolomite, xonotlite, perlite, vermiculite, Wollastonite, barite, magnesium carbonate, calcium hydroxide, calcium aluminates, silica, fumed silica, precipitated silica, aerogels, glass beads, hollow glass spheres, ceramic spheres, bauxite, comminuted concrete, and zeolites. The term "calcium carbonate" designates in the present document calcitic fillers produced from chalk, limestone or marble by grinding and/or precipitation.

[0092] According to one or more embodiments, the at least one filler is selected from the group consisting of calcium carbonate, calcium kaolins, diatomaceous earth, silica, fumed silica, and precipitated silica. According to one or more further embodiments, the moisture curing composition comprises at least two different fillers, preferably at least two different inert mineral fillers, preferably selected from the group consisting of calcium carbonate, calcium kaolins, diatomaceous earth, silica, fumed silica, and precipitated silica.

[0093] Preferably, the at least one filler has a median particle size d_{50} of not more than 100 μm , more preferably not more than 50 μm , most preferably not more than 25 μm . In particular, the median particle size d_{50} of the at least one filler is in the range of 0.5 - 100.0 μm , preferably 0.5 - 50.0 μm , more preferably 1.0 - 25.0 μm , most preferably 1.0 - 10.0 μm .

[0094] The term median particle size d_{50} designates in the present document the particle size below which 50% of all particles by volume are smaller than the d_{50} value. The term "particle size" designates the area-equivalent spherical diameter of a particle. The particle size distribution can be measured by laser diffraction according to the method as described in standard ISO 13320:2009. A Mastersizer 2000 device (trademark of Malvern Instruments Ltd, GB) can be used in measuring particle size distribution.

[0095] According to one or more embodiments, the at least one filler, preferably at least one inert mineral filler, is present in the moisture curing composition in an amount of at least 2.5 wt.-%, more preferably at least 10.0 wt.-%, most preferably at least 15.0 wt.-%, based on the total weight of the moisture curing composition. According to one or more further embodiments, the at least one filler, preferably at least one inert mineral filler, is present in the moisture curing composition in an amount of 5 - 75 wt.-%, preferably 10 - 70 wt.-%, more preferably 15 - 65 wt.-%, most preferably 20 - 60 wt.-%, based on the total weight of the moisture curing composition.

[0096] According to one or more embodiments, the moisture curing composition is a two-component composition composed of a first component A comprising:

- The at least one silane-terminated polymer,
- Optionally the at least one silane crosslinker, and
- Optionally at least one first filler, preferably at least one first inert mineral filler, and

5 a second component B comprising:

- Water,
- Optionally at least one second filler, preferably at least one second inert mineral filler, and
- Optionally at least one curing catalyst.

10

[0097] The at least one silane-terminated polymer, the at least one silane crosslinker, and the at least one first and/or second filler contained in the two-component moisture curing composition may be the same as those described above as components a), b), and c), including the preferred embodiments identified there.

15 **[0098]** According to one or more embodiments, the proportion of the at least one silane crosslinker is 0.1 - 15.0 wt.-%, preferably 0.5 - 10.0 wt.-%, based on the total weight of the first component **A**. It may be preferable that the first component **A** comprises at least two different silane crosslinkers.

[0099] According to one or more embodiments, the proportion of the at least one first filler is 0.5 - 25.0 wt.-%, preferably 1.0 - 20.0 wt.-%, based on the total weight of the first component **A**. It may be preferable that the first component **A** comprises at least two different fillers, preferably at least two different inert mineral fillers.

20 **[0100]** According to one or more embodiments, the weight ratio of the component **A** to component **B** is from 0.5:1 to 5:1, preferably from 1:1 to 3:1.

[0101] According to one or more embodiments, the proportion of water is 0.5 - 25.0 wt.-%, preferably 1.0 - 20.0 wt.-%, based on the total weight of the second component **B**.

25 **[0102]** According to one or more embodiments, the proportion of the at least one second filler is 1.0 - 65.0 wt.-%, preferably 10.0 - 55.0 wt.-%, based on the total weight of the second component **B**. It may be preferable that the second component **B** comprises at least two different fillers, preferably at least two different inert mineral fillers.

[0103] According to one or more embodiments, the second component **B** further comprises at least one curing catalyst.

30 **[0104]** Suitable curing catalysts to be used in the moisture curing composition include those which accelerate the reaction of the silane groups with moisture. These include, for example, organic titanium, tin, zirconium, aluminum, and phosphorus compounds. Particularly preferable as curing catalyst are organotitanates, organozirconates, organostannates, and organoaluminates. As organic ligands these catalysts can contain, in particular, alkoxy groups, sulfonate groups, carboxyl groups, dialkylphosphate groups, dialkylpyrophosphate and dialkyldiketonate groups.

35 **[0105]** Particularly suitable organotitanates include titanium(IV) complex compounds having two 1,3-diketonate ligands, especially 2,4-pentanedionate (i.e., acetylacetonate), and two alkoxide ligands; titanium(IV) complex compounds having two 1,3-ketoesterate ligands, more particularly ethyl acetoacetate, and two alkoxide ligands; titanium(IV) complex compounds having one or more amino alkoxide ligands, more particularly triethanolamine or 2-((2-aminoethyl)amino)ethanol, and one or more alkoxide ligands; titanium(IV) complex compounds having four alkoxide ligands; and organotitanates with higher degrees of condensation, especially oligomeric titanium(IV) tetrabutoxide, also referred to as polybutyl titanate.

40 **[0106]** Especially suitable as alkoxide ligands are isobutoxy, n-butoxy, isopropoxy, ethoxy, and 2-ethylhexoxy. Especially suitable are bis(ethylacetoacetato)diisobutoxytitanium(IV), bis(ethylacetoacetato)diisopropoxytitanium(IV), bis(acetylacetonato)diisopropoxytitanium(IV), bis(acetylacetonato)diisobutoxytitanium(IV), tris(oxyethyl)amineisopropoxytitanium(IV), bis[tris(oxyethyl)amine]diisopropoxytitanium(IV), bis(2-ethylhexane-1,3-dioxy)titanium(IV), tris[2-((2-aminoethyl)amino)ethoxy]ethoxytitanium(IV), bis(neopentyl(diallyl)oxydiethoxytitanium(IV), titanium(IV) tetrabutoxide, tetra-(2-ethylhexyloxy)titanate, tetra(isopropoxy)titanate, and polybutyl titanate.

45 **[0107]** Suitable organotitanates are commercially available under the trade name of Tyzor® AA, GBA, GBO, AA-75, AA-65, AA-105, DC, BEAT, BTP, TE, TnBT, KTM, TOT, TPT or IBAY (all from Du Pont / Dorf Ketel); under the trade name of Tytan® PBT, TET, X85, TAA, ET, S2, S4 or S6 (all from TensoChema), and under the trade name of Ken-React® KR® TTS, 7, 9QS, 12, 26S, 33DS, 38S, 39DS, 44, 134S, 138S, 133DS, 158FS or LICA® 44 (all from Kenrich Petrochemicals).

[0108] Suitable organozirconates are commercially available under the trade name of Ken-React® NZ® 38J, KZ® TPPJ, KZ® TPP, NZ® 01, 09, 12, 38, 44 or 97 (all from Kenrich Petrochemicals) and under the trade name of Snapcure® 3020, 3030, 1020 (all from Johnson Matthey & Brandenberger). A particularly suitable organoaluminate is the commercially available under the trade name of K-Kat® 5218 (from King Industries).

55 **[0109]** According to one or more embodiments, the proportion of the at least one curing catalyst is 0.1 - 10.0% by weight, preferably 0.5 - 7.5% by weight, even more preferably 1.0 - 5.0% by weight, most preferably 1.5 - 5.0% by weight, based on the total weight of the second component **B**.

[0110] According to one or more further embodiments, the moisture curing composition is a two-component composition

composed of a first component **A** comprising:

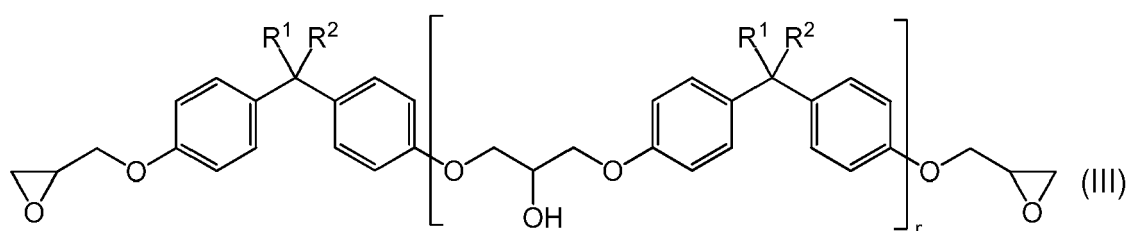
- The at least one silane-terminated polymer,
- At least one hardener or accelerator for epoxy resins,
- Optionally the at least one silane crosslinker, and
- Optionally at least one first filler, preferably at least one first inert mineral filler,

and a second component **B** comprising:

- At least one aqueous emulsion of at least one epoxy resin, and
- Optionally at least one second filler, preferably at least one second inert mineral filler.

[0111] The at least one silane-terminated polymer, the at least one silane crosslinker, and the at least one first and/or second filler contained in the two-component moisture curing composition may be the same as those described above as components a), b), and c), including the preferred embodiments identified there.

[0112] The at least one epoxy resin is preferably a liquid resin. Preferred liquid epoxy resins have the formula (III):



[0113] Here, the substituents R^1 and R^2 independently represent either H or CH_3 . In addition, the subscript r represents a value of 0 to 1. Preferably, r represents a value of ≤ 0.2 .

[0114] Thus these are preferably diglycidyl ethers of bisphenol A (DGEBA), bisphenol F and bisphenol A/F. The designation "A/F" here designates a mixture of acetone with formaldehyde, which is used as an educt in the production of bisphenol A/F. Suitable liquid resins, for example, are commercially available under the trade names Araldite® GY 250, Araldite® GY 282, Araldite® PY 304 from Huntsman International LLC, USA, or D.E.R.® 330 or D.E.R.® 331 from Dow Chemical Company, USA, or under the trade names Epikote® 828 or Epikote® 862 from Hexion Specialty Chemicals Inc., USA.

[0115] The term "aqueous emulsion" designates in the present document to emulsions having water as the main continuous (carrier) phase. Preferably, the term "aqueous" designates a 100% water carrier.

[0116] The at least one epoxy resin is typically present in the aqueous emulsion in an unmodified form. In particular, it is not modified for better emulsifiability, for example with a fatty acid.

[0117] The aqueous emulsion of at least one epoxy resin optionally contains at least one reactive diluent. Suitable reactive diluents include especially monofunctional epoxides, preferably glycidylated fatty alcohols.

[0118] Preferably the emulsion also contains at least one external emulsifier, especially a nonionic emulsifier, for example a fatty alcohol ethoxylate. The at least one external emulsifier may be present in the aqueous emulsion in an amount of not more than 10 wt.-%, preferably not more than 5 wt.-%, based on the total weight of the emulsion.

[0119] The emulsion preferably has a solids content of 60 to 90% by weight, especially of 70 to 90% by weight, preferably of 75 to 85%. Correspondingly, the aqueous emulsion of at least one epoxy resin may contain 10 - 40 % wt.-%, 10 - 30 wt.-%, preferably 15 - 25 wt.-%, of water, based on the total weight of the emulsion.

[0120] Preferably, the mean particle size (droplet diameter) of the at least one epoxy resin in the aqueous emulsion is in the range of 0.05 - 10 μm , in particular 0.1 - 7 μm , more preferably 0.2 - 5 μm .

[0121] The emulsion preferably has a narrow particle size distribution, wherein the size ratio of the largest to the smallest particle has a value in the range of ≤ 25 , preferably ≤ 20 . Especially the particle size distribution is such that 90% of the particles in the emulsion are smaller than 6 μm , preferably smaller than 4 μm , particularly preferably smaller than 3 μm . As a result of the small mean particle size and the narrow particle size distribution, the emulsion has a low tendency toward creaming or hardening and thus has a long storage life.

[0122] The preparation of the aqueous emulsion preferably takes place in a continuous process, especially using a stator-rotor mixer. Such a method is known to the person skilled in the art.

[0123] The first component **A** of the two-component composition further contains, in addition to the at least one silane-functional polymer, at least one hardener or accelerator for epoxy resins. These are in particular polyamines, for example isophorone diamine, m-xylylenediamine, polyether amines such as those that are commercially available under the trade

names of Jeffamine® (from Huntsman International LLC, USA), polyethylenimines, polyamidoamines, polyalkyleneamines such as diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA) or pentaethylenhexamine (PEHA), amine-epoxy adducts, pentamethyl diethylenetri-amine, N,N-dimethyl-N'-(dimethylaminopropyl)-1,3-propanediamine, bis(2-dimethylaminoethyl) ether, bis-(dimethylaminoethyl)-piperazine, N,N'-dimethylpiperazine; Mannich bases, for example dimethylaminomethylphenol, 2,4,6-tris(dimethylaminomethyl)phenol and 2,4,6-tris((3-(dimethylamino)propyl)-aminomethyl)phenol; polymercaptans, for example liquid mercaptan-terminated poly-sulfide polymers, such as those commercially available under the trade name of Thiokol® (from SPI Supplies, USA or from Toray Fine Chemicals, Japan), and under the trade name of Thioplast® (from Akzo Nobel NV, Netherlands); mercaptan-endcapped polyoxyalkylene derivatives, such as those available under the trade names of Capharden® (from Cognis GmbH, Germany), polyesters of thiocarboxylic acids such as pentaerythritol tetramercaptoacetate, trimethylolpropane trimercaptoacetate and glycol dimercaptoacetate, and aromatic polymercaptans such as 2,4,6-trimercapto-1,3,5-triazine; or imidazoles, for example imidazole, 1-methylimidazole, 1-ethylimidazole, 1-vinylimidazole, 2-methylimidazole, 2-ethylimidazole, 2-isopropylimidazole, 2-heptadecylimidazole, 2-phenylimidazole, 2-ethyl-4-methylimidazole, 1-benzyl-2-methylimidazole and 2,4-diamino-6-(2'-methylimidazolyl-(1'))-ethyl-s-triazine; and mixtures of the aforementioned hardeners or accelerators for epoxy resins.

[0124] In addition to the at least one hardener or accelerator mentioned, additional accelerators, especially phosphites, or acids, especially phosphoric acid and carboxylic acids, may be contained in the first component **A**.

[0125] Preferable as the at least one hardener or accelerator for epoxy resins are tertiary polyamines, especially pentamethyl-diethylene triamine, N,N-dimethyl-N'-(dimethylaminopropyl)-1,3-propanediamine, bis(2-dimethylaminoethyl)ether, bis-(dimethylaminoethyl)-piperazine, N,N'-dimethylpiperazine; Mannich bases, especially dimethylaminomethylphenol, 2,4,6-tris(dimethylaminomethyl)phenol and 2,4,6-tris((3-(dimethylamino)propyl)aminomethyl)phenol; as well as imidazoles, especially 1-methylimidazole, 1-ethylimidazole, 1-vinylimidazole, 2-methylimidazole, 2-ethylimidazole, 2-isopropylimidazole, 2-heptadecylimidazole, 2-ethyl-4-methylimidazole and 1-benzyl-2-methylimidazole. Particularly preferred are the Mannich bases mentioned.

[0126] According to one or more embodiments, the proportion of the at least one hardener or accelerator for epoxy resins is 0.5 - 25.0 wt.-%, preferably 1.0 - 20.0 wt.-%, based on the total weight of the first component **A**.

[0127] According to one or more further embodiments, the first component **A** comprises:

- The at least one silane-terminated polymer,
- The at least one hardener or accelerator for epoxy resins,
- The at least one silane crosslinker, and
- At least one first filler, preferably at least one first inert mineral filler.

[0128] The second component **B** comprises:

- At least one aqueous emulsion of at least one epoxy resin, and
- At least one second filler, preferably at least one second inert mineral filler.

[0129] In the embodiments, in which the second component **B** of the two-component moisture curing composition comprises at least one aqueous emulsion of at least one epoxy resin, it may be preferable that:

- The proportion of the at least one silane crosslinker is 1.0 - 15.0 wt.-%, preferably 1.5 - 10.0 wt.-%, based on the total weight of the first component **A** and/or
- The first component **A** comprises at least two different silane crosslinkers and/or
- The proportion of the at least one first filler, preferably at least one first inert mineral filler is 1.0 - 25.0 wt.-%, preferably 1.5 - 20.0 wt.-%, based on the total weight of the first component **A** and/or
- The first component **A** comprises at least two different fillers, preferably at least two different inert mineral fillers and/or
- The weight ratio of the component **A** to component **B** is from 0.5:1 to 5:1, preferably from 1:1 to 3:1 and/or
- The proportion of the at least one second filler, preferably at least one second inert mineral filler is 1.0 - 65.0 wt.-%, preferably 10.0 - 55.0 wt.-%, based on the total weight of the second component **B** and/or
- The second component **B** comprises at least two different fillers, preferably at least two different inert mineral fillers.

[0130] It is further preferred that the functional layer of the waterproofing membrane of the present invention is non-tacky at normal room temperature. Whether a surface of a specimen is tacky or not can be determined by pressing the surface with the thumb at a pressure of about 5 kg for 1 second and then trying to lift the specimen by raising the hand. In case the thumb does not remain adhered to the surface and the specimen cannot be raised up, the surface is considered to be non-tacky. In the context of the waterproofing membrane of the present invention, the "specimen" used in the tackiness test refers to a waterproofing membrane having a width of 10 cm and length of 20 cm.

[0131] The thickness of the functional layer is not particularly restricted and it may not be constant in the longitudinal and/or transverse direction of the sealing device. Preferably, the functional layer has a maximum thickness, determined by using the measurement method as defined in DIN EN 1849-2 standard, of 10 - 1000 μm , preferably 15 - 500 μm , even more preferably 25 - 250 μm , most preferably 50 - 200 μm . Furthermore, it may be advantageous that the functional layer has an average thickness, calculated as arithmetic average of the maximum and minimum thicknesses, determined by using the measurement method as defined in DIN EN 1849-2 standard, of 10 - 1000 μm , preferably 15 - 500 μm , even more preferably 25 - 250 μm , most preferably 50 - 200 μm .

[0132] The detailed composition of the barrier layer is not particularly restricted but should be as waterproof as possible and not to decompose or be mechanically damaged even under prolonged influence of water or moisture. Preferably, the barrier layer comprises at least one thermoplastic polymer, which is present in the barrier layer in an amount of at least 70 wt.-%, more at least 75 wt.-%, even more preferably at least 80 wt.-%, most preferably at least 85 wt.-%, based on the total weight of the barrier layer.

[0133] Suitable thermoplastic polymers to be used in the barrier layer include, for example, ethylene - vinyl acetate copolymer (EVA), ethylene - acrylic ester copolymers, ethylene - α -olefin co-polymers, ethylene - propylene co-polymers, polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET), polystyrene (PS), polyamides (PA), chloro-sulfonated polyethylene (CSPE), ethylene propylene diene rubber (EPDM), and polyisobutylene (PIB). It may be preferable that the at least one thermoplastic polymer is selected from the group consisting of low-density polyethylene, linear low-density polyethylene, high-density polyethylene, ethylene - vinyl acetate copolymer (EVA), ethylene - acrylic ester copolymers, ethylene - α -olefin co-polymers, and ethylene - propylene co-polymers.

[0134] The thickness of the barrier layer is not particularly restricted. The barrier layer may have a thickness, determined by using the measurement method as defined in DIN EN 1849-2 standard, of 0.1 - 5.0 mm, preferably 0.25 - 3.5 mm, more preferably 0.25 - 2.5 mm, most preferably 0.3 - 2.0 mm

[0135] According to one or more embodiments, the waterproofing membrane further comprises a connecting layer having first and second major surfaces and arranged between the barrier layer and the functional layer.

[0136] It may be preferred that at least a part of the first major surface of the connecting layer is directly connected to at least a part of the second major surface of the barrier layer and/or that at least a part of the second major surface of the connecting layer is directly connected to at least a part of the first major surface of the functional layer.

[0137] It may also be preferable that substantially the entire area of the first major surface of the connecting layer is directly connected to the second major surface of the barrier layer and/or that substantially the entire area of the second major surface of the connecting layer is directly connected to the first major surface of the functional layer. It may, for example, be preferable that at least 90%, more preferably at least 95%, of the first major surface of the connecting layer is directly connected to the second major surface of the barrier layer and/or that at least 90%, more preferably at least 95%, of the second major surface of the connecting layer is directly connected to the first major surface of the functional layer. Furthermore, it may also be preferable that the functional layer and the connecting layer have substantially the same width and length.

[0138] According to one or more embodiments, the connecting layer is composed of an at least partially cured film-forming curable composition comprising at least one epoxy resin and at least one hardener or accelerator for epoxy resins. According to one or more embodiments, the connecting layer is composed of a continuous layer of the at least partially cured film-forming curable composition.

[0139] The at least one epoxy resin contained in the film-forming curable composition is preferably a solid epoxy resin, more preferably a solid epoxy resin of the formula (III), wherein the substituents R^1 and R^2 independently is either H or CH_3 and the subscript r has a value of ≥ 1 , in particular ≥ 1.5 , more preferably in the range from 2 to 12.

[0140] Suitable hardeners and accelerators to be used in the curable composition include the ones discussed above related to the two-component moisture curing composition.

[0141] The curable composition may further comprise at least one silane chain extender or silane coupling agent. Suitable silane chain extenders and coupling agents include, for example vinyl trialkoxysilanes, 3-aminopropyl-dialkoxyalkylsilanes, 3-aminopropyl-trialkoxysilanes, N-(2-aminoethyl)-3-aminopropyl-dialkoxyalkylsilanes, N-(2-aminoethyl)-3-aminopropyl-trialkoxysilanes, 3-glycidoxypropyltrialkoxysilanes and 3-mercaptopropyl-trialkoxysilanes. Particularly suitable silane chain extenders and silane coupling agents include vinyl trimethoxysilane, vinyl triethoxysilane, 3-aminopropyl-trimethoxysilane, 3-aminopropyl-triethoxysilane, N-(2-aminoethyl)-3-aminopropyl-dimethoxymethylsilane, N-(2-aminoethyl)-3-aminopropyl-trimethoxysilane, N-(2-aminoethyl)-3-aminopropyl-triethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropyltriethoxysilane, 3-mercaptopropyl-trimethoxysilane and 3-mercaptopropyl-triethoxysilane.

[0142] The curable composition may further comprise at least one organic solvent. The term "organic solvent" designates in the present document non- aqueous solvents and combinations of non-aqueous solvents, and, in particular, to solvents comprising organic compounds. Preferably, the at least one organic solvent is selected from the group consisting of toluene, xylene, hexane, octane, and mixtures thereof.

[0143] According to one or more embodiments, the film-forming curable composition comprises at least 10 wt.-%, preferably at least 20 wt.-%, more preferably at least 35 wt.-% of at least one solid epoxy resin, based on the total weight of the curable composition. It may be preferable that the film-forming curable composition comprises 15 - 75 wt.-%, more preferably 25 - 65 wt.-% of at least one solid epoxy resin, based on the total weight of the film-forming curable composition.

[0144] According to one or more embodiments, the film-forming curable composition comprises:

- 0.1 - 10 wt.-%, preferably 0.5 - 7.5 wt.-% of the at least one hardener or accelerator for epoxy resins, based on the total weight of the film-forming curable composition and/or
- 0.1 - 10 wt.-%, preferably 0.5 - 7.5 wt.-% of the at least one silane chain extender or silane coupling agent, based on the total weight of the film-forming curable composition and/or
- 5.0 - 50.0 wt.-%, preferably 15.0 - 45.0 wt.-% of the at least one organic solvent, based on the total weight of the film-forming curable composition

[0145] According to one or more further embodiments, the connecting layer is a thermoplastic polymer layer comprising at least 80 wt.-% of at least one thermoplastic polymer.

[0146] The at least one thermoplastic polymer is preferably ethyl vinyl acetate copolymer, more preferably ethyl vinyl acetate copolymer having a content of a structural unit derived from vinyl acetate (hereinafter referred to as "vinyl acetate unit") of at least 30 wt.-%, more preferably at least 35 wt.-%, most preferably at least 40 wt.-%.

[0147] According to one or more further embodiments, the connecting layer is composed of a pressure sensitive adhesive (PSA) composition or pressure sensitive hot-melt adhesive (HM-PSA) composition.

[0148] Suitable pressure sensitive adhesives include compositions based on acrylic polymers, styrene block copolymers, amorphous poly- α -olefins (APAO), vinyl ether polymers, elastomers such as, for example, butyl rubber, ethylene vinyl acetate, natural rubber, nitrile rubber, silicone rubber, and ethylene-propylene-diene rubber. In addition to the above mentioned polymers, suitable pressure sensitive adhesive compositions typically comprise one or more additional constituents including, for example, tackifying resins, waxes, and plasticizers as well as one or more additives such as, for example, UV-light absorption agents, UV- and heat stabilizers, optical brighteners, pigments, dyes, and desiccants.

[0149] According to one embodiment, the adhesive is a styrene block copolymer-based pressure sensitive adhesive or styrene block copolymer-based pressure sensitive hot-melt adhesive comprising at least one styrene block copolymer.

[0150] Suitable styrene block copolymers include block copolymers of the SXS type, in each of which S denotes a non-elastomer styrene (or polystyrene) block and X denotes an elastomeric α -olefin block, which may be polybutadiene, polyisoprene, polyisoprene-polybutadiene, completely or partially hydrogenated polyisoprene (poly ethylene-propylene), completely or partially hydrogenated polybutadiene (poly ethylene-butylene). The elastomeric α -olefin block preferably has a glass transition temperature in the range from -55°C to - 35°C. The elastomeric α -olefin block may also be a chemically modified α -olefin block. Particularly suitable chemically modified α -olefin blocks include, for example, maleic acid-grafted α -olefin blocks and particularly maleic acid-grafted ethylene-butylene blocks.

[0151] Preferably, the at least one styrene block copolymer is selected from the group consisting of SBS, SIS, SIBS, SEBS, and SEPS block copolymers. These can have a linear, radial, diblock, triblock or star structure, linear structure being preferred. Suitable styrene block copolymers of the SXS type include block copolymers based on saturated or unsaturated middle blocks X. Hydrogenated styrene block copolymers are also suitable. The at least one styrene block copolymer may be present in the adhesive in an amount of 5 - 60 wt.-%, more preferably 10 - 55 wt.-%, most preferably 20 - 50 wt.-%, based on the total weight of the adhesive.

[0152] The styrene block copolymer-based pressure sensitive adhesive preferably comprises at least one tackifying resin. The term "tackifying resin" designates in the present document resins that in general enhance the adhesion and/or tackiness of an adhesive composition. The term "tackiness" designates in the present document the property of a substance of being sticky or adhesive by simple contact. The tackiness can be measured, for example, as a loop tack. Preferred tackifying resins are tackifying at a temperature of 25°C.

[0153] Suitable tackifying resins include synthetic resins, natural resins, and chemically modified natural resins. The at least one tackifying resin may be present in the styrene block copolymer based pressure sensitive adhesive in an amount of 5 - 60 wt.-%, preferably 10 - 55 wt.-%, most preferably 20 - 50 wt.-%, based on the total weight of the adhesive.

[0154] Examples of suitable natural resins and chemically modified natural resins include rosins, rosin esters, phenolic modified rosin esters, and terpene resins. The term "rosin" is to be understood to include gum rosin, wood rosin, tall oil rosin, distilled rosin, and modified rosins, for example dimerized, hydrogenated, maleated and/or polymerized versions

of any of these rosins.

[0155] Suitable terpene resins include copolymers and terpolymers of natural terpenes, such as styrene/terpene and alpha methyl styrene/terpene resins; polyterpene resins obtainable from the polymerization of terpene hydrocarbons, such as the bicyclic monoterpene known as pinene, in the presence of Friedel-Crafts catalysts at moderately low temperatures; hydrogenated polyterpene resins; and phenolic modified terpene resins including hydrogenated derivatives thereof.

[0156] The term "synthetic resin" designates in the present document compounds obtained from the controlled chemical reactions such as polyaddition or polycondensation between well-defined reactants that do not themselves have the characteristic of resins. Monomers that may be polymerized to synthesize the synthetic resins may include aliphatic monomer, cycloaliphatic monomer, aromatic monomer, or mixtures thereof. Aliphatic monomers can include C₄, C₅, and C₆ paraffins, olefins, and conjugated diolefins. Examples of aliphatic monomers or cycloaliphatic monomers include butadiene, isobutylene, 1,3-pentadiene, 1,4-pentadiene, cyclopentane, 1-pentene, 2-pentene, 2-methyl-1-pentene, 2-methyl-2-butene, 2-methyl-2-pentene, isoprene, cyclohexane, 1-3-hexadiene, 1-4-hexadiene, cyclopentadiene, and dicyclopentadiene. Aromatic monomers can include C₈, C₉, and C₁₀ aromatic monomer, such as styrene, indene, derivatives of styrene, derivatives of indene, coumarone and combinations thereof.

[0157] In particular, suitable synthetic resins include synthetic hydrocarbon resins made by polymerizing mixtures of unsaturated monomers that are obtained as by-products of cracking of natural gas liquids, gas oil, or petroleum naphthas. Synthetic hydrocarbon resins obtained from petroleum based feedstocks are referred in the present document as "petroleum hydrocarbon resins". These include also pure monomer aromatic resins, which are made by polymerizing aromatic monomer feedstocks that have been purified to eliminate color causing contaminants and to precisely control the composition of the product. Petroleum hydrocarbon resins typically have a relatively low average molecular weight (M_n), such in the range of 250 - 5'000 g/mol and a glass transition temperature of above 0°C, preferably equal to or higher than 15°C, more preferably equal to or higher than 30°C.

[0158] It may be preferable that the at least one tackifying resin is selected from the group consisting of C5 aliphatic petroleum hydrocarbon resins, mixed C5/C9 aliphatic/aromatic petroleum hydrocarbon resins, aromatic modified C5 aliphatic petroleum hydrocarbon resins, cycloaliphatic petroleum hydrocarbon resins, mixed C5 aliphatic/cycloaliphatic petroleum hydrocarbon resins, mixed C9 aromatic/cycloaliphatic petroleum hydrocarbon resins, mixed C5 aliphatic/cycloaliphatic/C9 aromatic petroleum hydrocarbon resins, aromatic modified cycloaliphatic petroleum hydrocarbon resins, and C9 aromatic petroleum hydrocarbon resins as well hydrogenated versions of the aforementioned resins. The notations "C5" and "C9" indicate that the monomers from which the resins are made are predominantly hydrocarbons having 4-6 and 8-10 carbon atoms, respectively. The term "hydrogenated" includes fully, substantially and at least partially hydrogenated resins. Partially hydrogenated resins may have a hydrogenation level, for example, of 50%, 70%, or 90%.

[0159] Preferred thickness of the connecting layer depends on the composition of the connecting layer and it may not be constant in the longitudinal and/or transverse direction of the waterproofing membrane.

[0160] In case the connecting layer is composed of a cured material of a curable solvent-based epoxy resin composition, it may be preferable that it has a maximum thickness of, determined by using the measurement method as defined in DIN EN 1849-2 standard, of 10 - 1000 µm, preferably 15 - 500 µm, even more preferably 25 - 350 µm, most preferably 50 - 250 µm. Furthermore, it may be advantageous that the connecting layer has an average thickness, calculated as arithmetic average of the maximum and minimum thicknesses, determined by using the measurement method as defined in DIN EN 1849-2 standard, of 10 - 1000 µm, preferably 15 - 500 µm, even more preferably 25 - 350 µm, most preferably 50 - 250 µm.

[0161] In case the connecting layer is a thermoplastic polymer layer, it may be preferable that it has a maximum thickness, determined by using the measurement method as defined in DIN EN 1849-2 standard, of 10 - 1000 µm, preferably 15 - 500 µm, even more preferably 25 - 350 µm, most preferably 50 - 250 µm. Furthermore, it may be advantageous that the connecting layer has an average thickness, calculated as arithmetic average of the maximum and minimum thicknesses, determined by using the measurement method as defined in DIN EN 1849-2 standard, of 10 - 1000 µm, preferably 15 - 500 µm, even more preferably 25 - 350 µm, most preferably 50 - 250 µm.

[0162] In case the connecting layer is composed of a pressure sensitive adhesive composition, it may be preferable that it has a maximum thickness, determined by using the measurement method as defined in DIN EN 1849-2 standard, of 50 - 1500 µm, preferably 100 - 1000 µm, even more preferably 150 - 1000 µm, most preferably 250 - 750 µm. Furthermore, it may be advantageous that the connecting layer has an average thickness, calculated as arithmetic average of the maximum and minimum thicknesses, determined by using the measurement method as defined in DIN EN 1849-2 standard, of 50 - 1500 µm, preferably 100 - 1000 µm, even more preferably 150 - 1000 µm, most preferably 250 - 750 µm.

[0163] The second major surface of the barrier layer may have been subjected to a pre-treatment step in order to improve the bonding of the barrier layer to the functional layer or to the connecting layer, if used. Suitable pre-treatment steps include, for example, air-pressure plasma treatment, wet chemical functional grafting, and oxo-fluorination.

[0164] Air pressure plasma-treatment can be used to clean the surface of the barrier layer from organic pollution and/or

to increase the free surface energy. The air pressure plasma-treatment can be conducted using conventional techniques known to a person skilled in the art.

[0165] In wet chemical functional grafting, a grafting compound, such as a silane compound is grafted upon the molecules of the material of the barrier layer to increase the free surface energy and/or to improve bonding with the functional layer. In case a silane grafting solution is used, silicon is covalently bonded to the material of the membrane and it can act as a link between the barrier layer and the functional layer containing silane-terminated polymers. The silane grafting solution used in the functional grafting is typically a solvent-based solution of at least one organic silane, such as organoalkoxysilane or aminoalkyl organoalkoxysilane, and at least one free-radical initiator. The free-radical initiator can be heat activated, such as peroxide initiator, or a UV-radiation activated, such as a benzophenone.

[0166] In an oxo-fluorination treatment, the surface of the barrier layer is first subjected to a fluorination treatment to provide a surface fluorinated barrier layer, which is subsequently treated with an oxidant fluid to oxidize the fluorinated surface. The fluorination and oxidation steps may also be conducted in simultaneously in one single treatment step. The stability of the oxidized surface fluorinated barrier layer may further be improved by treating the surface with an antioxidant, such as nitrogen dioxide, nitric oxide, dinitrogen dioxide, dinitrogen trioxide, dinitrogen tetroxide, sulfur dioxide, or sulfur trioxide.

[0167] The waterproofing membrane may further comprise a reinforcement layer in order to improve the dimensional stability of the membrane. The reinforcement layer is preferably at least partially embedded into the barrier layer. Suitable reinforcement layers include, for example, reinforcing scrim and reinforcing fiber materials.

[0168] Any kind of reinforcing scrim commonly used for improving the dimensional stability of thermoplastic waterproofing membranes can be used. Typically such reinforcing scrim comprise a mesh of interwoven strands, which comprises or are composed of plastic or metal material. Suitable reinforcing scrim have a tensile strength sufficient to resist tearing when exposed to typical tensile loads experienced by waterproofing membranes from various directions. Particularly suitable materials for the reinforcing scrim layer include, for example, polypropylene, polyethylene terephthalate (PET), and polyester.

[0169] The term "fiber material" designates in the present document materials composed of fibers. The fibers can comprise or consist of organic or synthetic material. These include, in particular, cellulose fibers, cotton fibers, protein fibers, synthetic organic fibers, and synthetic inorganic fibers. Suitable synthetic fibers include fibers made of polyester, a homopolymer or copolymer of ethylene and/or propylene, viscose, nylon, and glass. The fibers can be short fibers or long fibers, spun, woven or unwoven fibers or filaments. The fibers can moreover be aligned or drawn fibers. Moreover, it may be advantageous to use different fibers, both in terms of geometry and composition, together. The reinforcing fiber material can be in the form of a fiber mat, a nonwoven fabric, or a fibrous tissue. Particularly suitable materials for the reinforcing fiber material include glass fibers, polyester fibers, and nylon fibers.

[0170] According to one or more embodiments, the waterproofing membrane comprises a reinforcement layer, which is fully embedded into the barrier layer. By the expression "fully embedded" is meant that the reinforcement layer is substantially fully covered by the matrix of the barrier layer.

[0171] Another subject of the present invention is a method for producing a waterproofing membrane of the present invention, the method comprising steps of:

i) Providing a moisture curing composition comprising the constituents as defined above,

ii) Applying the moisture curing composition in a fluid state to at least a part of the second major surface of the barrier layer or to at least a part of the second major surface of the connecting layer, if present, to form a layer of the moisture curing composition,

iii) Allowing the applied moisture curing composition to cure to form a layer of at least partially cured moisture curing composition.

[0172] In case the moisture curing composition is a multiple-component composition, step i) is conducted by mixing the components A and B of the multiple-component composition with each other.

[0173] The moisture curing composition may be applied to the surface of the barrier layer or connecting layer, if present, by using any conventional means such as by die coating, extrusion coating, roller coating, or by spray lamination techniques.

[0174] According to one or more embodiments, the moisture curing composition is applied in fluid state to at least a part of the second surface of a connecting layer and the method comprises a further step of:

i') Providing a composition of the connecting layer with the constituents as defined above and applying the composition to at least a part of the second major surface of the barrier layer to form a layer of the composition.

[0175] The barrier layer can be produced by using any conventional technology suitable for producing thermoplastic membranes. The barrier layer can be produced, for example, by using conventional extruding, calendering, compressing,

or casting techniques. It goes without saying that the step i') precedes the step ii).

[0176] The moisture curing composition may be applied only on a part or on substantially the entire area of the second major surface of the barrier layer or of the connecting layer. It may also be preferable that the moisture curing composition is applied over substantially the entire area of the second major surface of the barrier layer or of the connecting layer. It may, for example, be preferable that the moisture curing composition is applied over at least 80%, more preferably at least 90%, most preferably at least 95%, of the area of the second major surface of the barrier layer or of the connecting layer.

[0177] Another subject of the present invention is a method for waterproofing a substrate comprising steps of:

i") Applying a waterproofing membrane of the present invention to a surface of the substrate such that the first major surface of the barrier layer is directed against the surface of the substrate,

ii") Casting a fresh cementitious composition on the second major surface of the functional layer,

iii") Allowing the fresh cementitious composition to harden.

[0178] The term "cementitious composition" designates concrete, shotcrete, grout, mortar, paste or a combination thereof. The terms "paste", "mortar", "concrete", "shotcrete", and "grout" are well-known terms in the State-of-the-Art. Pastes are mixtures comprising a hydratable cement binder, usually Portland cement, masonry cement, or mortar cement. Mortars are pastes additionally including fine aggregate, for example sand. Concrete is a mortar additionally including coarse aggregate, for example crushed gravel or stone. Shotcrete is concrete (or sometimes mortar) conveyed through a hose and pneumatically projected at high velocity onto a surface. Grout is a particularly flowable form of concrete used to fill gaps.

[0179] Cementitious compositions can be formed by mixing required amounts of certain components, for example, a hydratable cement, water, and fine and/or coarse aggregate, to produce the particular cementitious composition. The term "fresh cementitious composition" or "liquid cementitious composition" designate cementitious compositions before hardening, particularly before setting.

[0180] The casted cementitious composition after hardening can be part of a structure, in particular, an above-ground or underground structure, for example a building, garage, tunnel, landfill, water retention, pond, dike or an element for use in pre-fabricated constructions.

[0181] Another subject of the present invention is a waterproofed construction comprising a layer of concrete and a waterproofing membrane according to the present invention arranged between a surface of a substrate and the layer of concrete such that the first surface of the barrier layer is directed against the surface of the substrate and the second surface of the functional layer is bonded to the layer of concrete.

[0182] Still another subject of the present invention is the use of the waterproofing membrane of the present invention for sealing of under and above ground structures against water penetration.

Detailed description of the Drawings

[0183] Fig. 1 shows a cross-section of a waterproofing membrane (1) comprising a barrier layer (2) having first and second opposed major surfaces and a functional layer (3) having first and second opposed major surfaces. In this embodiment, substantially the entire first major surface of the functional layer (3) is directly connected to the second major surface of the barrier layer (2).

[0184] Fig. 2 shows cross-section of a waterproofing membrane (1) comprising a barrier layer (2), a functional layer (3), and a connecting layer (4) arranged between the barrier layer (2) and the functional layer (3). In this embodiment, substantially the entire first major surface of the connecting layer (4) is directly connected to the second major surface of the barrier layer (2) and substantially the entire second major surface of the connecting layer (4) is directly connected to the first major surface of the functional layer (2).

[0185] Fig. 3 shows a cross-section of a waterproofed construction comprising a substrate (5) and a layer of concrete (6) and a waterproofing membrane (1) arranged between the outer surface of the substrate (5) and the layer of concrete (6) such that the first surface of the barrier layer (2) is directed against the outer surface of the substrate and the second surface of the functional layer is bonded to the layer of concrete (6).

Examples

[0186] The followings compounds and products were used in the examples:

Table 1

5	Geniosil® STP-E15	Silane-terminated polymer	Wacker Chemie AG, Germany
	Silquest® A-171	Vinyl silane	Momentive Performance Materials Inc., USA
10	Silquest® A-1110	3-Aminopropyl-trimethoxysilane	Momentive Performance Materials Inc., USA
	Jeffamine® D-230	Amine hardener for epoxy resins	Huntsmann International LLC
15	Omyacarb® 5GU	Calcium carbonate filler	Omya AG, Switzerland
	Araldite® GY 250	Liquid epoxy resin	Huntsmann International LLC
20	DBTDL in DIDP	Dibutyltin dilaurate dissolved in diisodecyl phthalate (4 wt.-%)	Sigma Aldrich, Switzerland
	Aerosil® R200	Fumed silica filler	Evonik Industries
	Araldite®GZ 7071 X75	Medium molecular weight liquid epoxy resin in xylene	Huntsmann International LLC
25	Jeffamine® D-400	Amine hardener for epoxy resins	Huntsmann International LLC
	Dynasylan® AMEO	3-Aminopropyltriethoxysilane	Evonik Industries

Preparation of the sample waterproofing membranes

[0187] The sample waterproofing membranes were prepared by applying the composition of a functional layer or the composition of the connecting layer, if applicable, to one of the outer surfaces of a thermoplastic barrier layer.

[0188] Two different thermoplastic waterproofing products, WT-1210-06-HF and Combiflex SG (both from Sika Schweiz AG), were used as the thermoplastic barrier layer. The first one is an ethylene vinyl acetate copolymer (EVA) based waterproofing membrane and the second one is a waterproofing tape based on ethylene-propylene copolymer. Surfaces of both types of barrier layers have been subjected to oxo-fluorination treatment.

[0189] The compositions of the functional layer were applied on the surface of the barrier layer or connecting layer using a K-control coater (from Erichsen) and constant coating speed of 1 m/min. The thickness of the applied layer was controlled by wire bars. After the application, the composition of the functional layer was allowed to cure at normal room temperature (23°C, relative humidity of 50%).

[0190] In examples Ref-1, Ex-1 - Ex-8, and Ex-10, an epoxy resin-based connecting layer was applied on the barrier layer before application of the composition of the functional layer. The epoxy resin-based layer was applied with a coating thickness of 100 µm using a K-control coater (from Erichsen) and constant coating speed of 1 m/min. After the application, the connecting layer was allowed to cure at normal room temperature (23°C, relative humidity of 50%).

[0191] The build-up of the sample membranes is shown in Table 3.

Preparation of the moisture curing composition, functional layer

[0192] The moisture curing compositions were produced by adding the ingredients of the components A and B as shown in Table 2 to a speed mixer and mixing the contents using a mixing speed of 1000 rounds per minute until a homogeneous mixture was obtained. The moisture curing composition of example FL-1 is a one-component composition (only component A) whereas the compositions FL-2 to FL-8 are two-component moisture curing compositions.

[0193] The "STP-S" silane-terminated polymer contained in compositions FL2- to FL-8 was prepared as follows: 1000 g polyol (Acclaim® 12200, low monol polyoxypropylene diol from Covestro; OH-number 11.0 mg KOH/g; water content ca. 0.02 wt.-%), 35.2 g isophorone diisocyanate (Vestanat® IPDI from Evonik Industries), 122.5 g diisodecyl phthalate, and 0.12 g dibutyltin dilaurate were heated under exclusion of moisture and with continuous stirring to a

temperature of 90°C and kept at this temperature until the content of free isocyanate groups, determined by titrimetry, reached a value of 0.39 wt.-%. Subsequently, 36.9 g N-(3-trimethoxysilylpropyl)aminosuccinic acid diethyl ester were added and the stirring was continued until no free isocyanate groups were detected by FT-IR spectroscopy. The produced silane-terminated polymer was cooled to room temperature and stored under the exclusion of moisture.

Preparation of the film-forming curable composition, connecting layer

[0194] The film-forming curable composition was produced adding the ingredients of the composition as presented below to a speed mixer and mixing the contents using a mixing speed of 1000 rounds per minute until a homogeneous mixture was obtained.

[0195] The film-forming curable composition contained:

- 53.9 wt.-% of Araldite GZ 7071 X75 (amount without solvent)
- 4.88 wt.-% of Jeffamine D-400,
- 4.69 wt.-% of Dynasylan AMEO, and
- 36.52 wt.-% of xylene

Peel resistance measurement

[0196] The concrete adhesion strength of the exemplary waterproofing membranes was tested by measuring the 90° peel resistance from a cured concrete surface. For the determination of the peel resistance, concrete specimen having a sample membrane adhered on its surface were first prepared as follows.

[0197] A sample membrane having dimensions of 15 cm x 15 cm was prepared with respective barrier, functional layer, and connecting layer, if applicable. One edge of the sample membrane on the side of the functional layer was covered with an adhesive tape to prevent the adhesion to the hardened concrete. The membrane was dried for at least one week and placed into a framework having approximately the same width and length as the membrane with the functional layer facing upwards and the barrier layer against the bottom of the framework.

[0198] A batch of fresh concrete formulation having a water-cement ratio of 0.44 was then prepared by mixing the following ingredients:

- 32.1 wt.-% of cement (CEM I 42.5 N)
- 46.3 of sand having particles size range of 0 - 1 mm,
- 14.3 wt.-% of water,
- 7.1 wt.-% of limestone filler Nekafill®-15 (from KFN), and
- 2.2 wt.-% of Viscocrete® 3082 (from Sika Schweiz AG).

[0199] The formworks containing the sample membranes were subsequently filled with the fresh concrete formulation such that the membrane was bonded with the concrete on the side of the functional layer. The casted concrete was allowed to cure for one day covered with a polyethylene foil. The film was then removed and the concrete block was stripped from the framework and stored in wet room (23°C, 95% relative humidity) for 28 days to complete the hydration of the cement. The membrane was then cut into three stripes with a gap of approximately 1 cm between the stripes for measurement of peel resistances.

[0200] The measurement of peel resistances of the sample membranes from the concrete block was conducted in accordance with the procedure laid out in the standard DIN EN 1372:2015-06. A Zwick Roell AllroundLine Z010 material testing apparatus equipped with a Zwick Roell 90°-peeling device (type number 316237) was used for conducting the peel resistance measurements.

[0201] In the peel resistance measurement, the membrane was peeled off from the surface of the concrete block at a peeling angle of 90° and at a constant cross beam speed of 100 mm/min at normal room temperature and humidity (23°C, 50% relative humidity). The values for peel resistance were calculated as average peel force per width of the sample membrane [N/ 50 mm] during peeling excluding the first and last quarter of the total peeling length from the calculation. The average peel resistances shown in Table 2 and 3 are calculated based on measurements obtained with three strips of the same sample membrane.

Table 2

Composition [pbw]	FL-1	FL-2	FL-3	FL-4	FL-5	FL-6	FL-7	FL-8
Component A								

EP 3 546 541 A1

(continued)

Composition [pbw]	FL-1	FL-2	FL-3	FL-4	FL-5	FL-6	FL-7	FL-8
Geniosil STP-E15	94.00	-	-	-	-	-	-	-
STP-S	-	80.00	68.00	80.00	80.00	80.00	80.00	80.00
Silquest A-171	-	5.00	4.25	5.00	5.00	5.00	5.00	5.00
Silquest A-1110	6.00	2.00	1.70	2.00	2.00	2.00	2.00	2.00
Jeffamine D-230	-	-	15.47	18.20	18.20	18.20	9.58	31.93
Omyacarb 5GU	-	49.74	0.00	94.80	32.80	197.00	76.00	126.00
Component B								
Araldite GY 250	-	-	57.00	57.00	57.00	57.00	30.00	100.00
Water	-	10.00	4.00	10.00	10.00	10.00	10.00	10.00
DBTDL in DIDP	-	1.00	0.00	0.00	0.00	0.00	0.00	0.00
Omyacarb 5GU	-	16.26	0.00	31.00	10.70	64.40	25.00	41.00
Aerosil R200	-	2.00	0.00	2.00	2.00	2.00	2.00	2.00
Total	100.00	166.00	150.42	300.00	217.70	435.60	239.58	397.93
Concrete adhesion strenght, after 28 days [N/50 mm]	27	21	21	55	34	21	43	37

Table 3

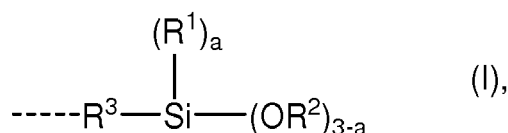
Build-up of membrane	Ref-1	Ex-1	Ex-2	Ex-3	Ex-4	Ex-5	Ex-6	Ex-7	Ex-8	Ex-9	Ex-10
Barrier layer	EVA	EVA	EVA	EVA	EVA	EVA	EVA	EVA	EVA	E-P	E-P
Thickness [mm]	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	1	1
Surface modification	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Connecting layer	Epoxy	Epoxy	Epoxy	Epoxy	Epoxy	Epoxy	Epoxy	Epoxy	Epoxy	No	Epoxy
Thickness [mm]	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	-	0.1
Functional layer	No	FL-1	FL-2	FL-3	FL-4	FL-5	FL-6	FL-7	FL-8	FL-4	FL-4
Thickness [mm]	-	0.1	0.1	0.1	0.1	0.1	0.1	0.1	1.1	0.1	0.1
Concrete adhesion strenght, after 28 days [N/50 mm]	0	27	21	21	55	34	21	43	37	24	57

Claims

1. A waterproofing membrane (1) comprising a barrier layer (2) having first and second major surfaces and a functional layer (3) having first and second major surfaces, wherein the functional layer (3) and the barrier layer (2) are directly or indirectly connected over at least a part of their opposing major surfaces and wherein the functional layer (3) is composed of an at least partially cured moisture curing composition comprising:

- a) At least one silane-terminated polymer and
b) Optionally at least one silane crosslinker.

2. The waterproofing membrane according to claim 1, wherein the at least one silane-terminated polymer has at least one terminal group of formula (I):



wherein

R¹ is an alkyl-group having 1 to 8 C atoms,
R² is an acyl or alkyl group having 1 to 5 C atoms,
R³ is a linear or branched, or cyclic, alkylene group having 1 to 12 C atoms, optionally with aromatic moieties, and optionally with 1 or more heteroatoms, and
a is 0 or 1 or 2, preferably 0,
and/or wherein the at least one silane-terminated polymer is a silane-terminated polyurethane polymer.

3. The waterproofing membrane according to any one of claims 1 or 2, wherein the at least one silane-terminated polymer is present in the moisture curing composition in an amount of 5 - 85 wt.-%, preferably 10 - 75 wt.-%, based on the total weight of the moisture curing composition.
4. The waterproofing membrane according to any one of the previous claims, wherein the moisture curing composition comprises at least one silane crosslinker selected from the group consisting of aminosilanes, epoxysilanes, mercaptosilanes, (meth)acrylosilanes, and vinyl silanes and/or wherein the at least one silane crosslinker is present in the moisture curing composition in an amount of 0.5 - 10.0 wt.-%, preferably 1.0 - 7.5 wt.-%, based on the total weight of the moisture curing composition.
5. The waterproofing membrane according to any one of the previous claims, wherein the moisture curing composition further comprises:
c) At least one filler, preferably at least one inert mineral filler.
6. The waterproofing membrane according to claim 5, wherein the at least one filler is present in the moisture curing composition in an amount of 5 - 75 wt.-%, preferably 10 - 70 wt.-%, based on the total weight of the moisture curing composition.
7. The waterproofing membrane according to any one of the previous claims, wherein the moisture curing composition is a two-component composition composed of a first component A comprising:

- The at least one silane-terminated polymer,
- Optionally the at least one silane crosslinker, and
- Optionally at least one first filler, preferably at least one first inert mineral filler,

and a second component B comprising:

- Water,
- Optionally at least one second filler, preferably at least one second inert mineral filler, and
- Optionally at least one curing catalyst, preferably selected from the group consisting of organotitanates, or-

ganozirconates, organostannates, and organoaluminates

8. The waterproofing membrane according to any one of claims 1-6, wherein the moisture curing composition is a two-component composition composed of a first component **A** comprising:

- The at least one silane-terminated polymer,
- At least one hardener or accelerator for epoxy resins,
- Optionally the at least one silane crosslinker, and
- Optionally at least one first filler, preferably at least one first inert mineral filler,

and a second component **B** comprising:

- At least one aqueous emulsion of at least one epoxy resin, preferably at least one liquid epoxy resin, and
- Optionally at least one second filler, preferably at least one second inert mineral filler.

9. The waterproofing membrane according to claim 8, wherein the aqueous emulsion of the at least one epoxy resin comprises 10 - 40% wt.-%, preferably 15 - 25 wt.-% of water, based on the total weight of the aqueous emulsion.

10. The waterproofing membrane according to any one of claims 7-9, wherein the weight ratio of the component **A** to the component **B** is from 0.5:1 to 5:1, preferably from 1:1 to 3:1.

11. The waterproofing membrane according to any one of the previous claims further comprising a connecting layer (4) having first and second major surfaces, wherein at least a part of the first major surface of the connecting layer (4) is directly connected to at least a part of the second major surface of the barrier layer (2) and/or at least a part of the second major surface of the connecting layer (4) is directly connected to at least a part of the first major surface of the functional layer (3).

12. The waterproofing membrane according to claim 11, wherein the connecting layer (4) is composed of an at least partially cured film-forming curable composition comprising at least one epoxy resin and at least one hardener or accelerator for epoxy resins.

13. The waterproofing membrane according to claim 12, wherein the film-forming curable composition comprises 15 - 75 wt.-%, preferably 25 - 65 wt.-% of at least one solid epoxy resin, based on the total weight of the film-forming curable composition.

14. A method for producing a waterproofing membrane according to any one of the previous claims comprising steps of:

- i) Providing a moisture curing composition comprising the constituents as defined in any one of the previous claims,
- ii) Applying the moisture curing composition in a fluid state to at least a part of a second major surface of a barrier layer or to at least a part of a second major surface of a connecting layer, if present, to form a layer of the moisture curing composition,
- iii) Allowing the applied moisture curing composition to cure to form a layer of an at least partially cured moisture curing composition.

15. A method for waterproofing a substrate comprising the steps of:

- i") Applying a waterproofing membrane according to any one of claims 1-13 to a surface of the substrate such that the first major surface of the barrier layer is directed against the surface of the substrate,
- ii") Casting a fresh cementitious composition on the second major surface of the functional layer,
- iii") Allowing the fresh cementitious composition to harden.

16. A waterproofed construction comprising a layer of concrete (6) and a waterproofing membrane (1) according to any one of claims 1-13 arranged between a surface of a substrate (5) and the layer of concrete (6) such that the first surface of the barrier layer (2) is directed against the surface of the substrate (5) and the second surface of the functional layer (3) is bonded to the layer of concrete (6).

17. Use of the waterproofing membrane according to any one of claims 1-13 for sealing of under and above ground

structures against water penetration.

5

10

15

20

25

30

35

40

45

50

55

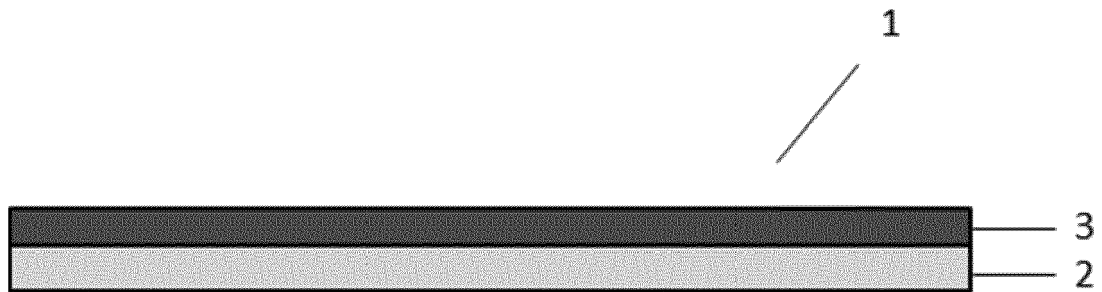


Fig. 1

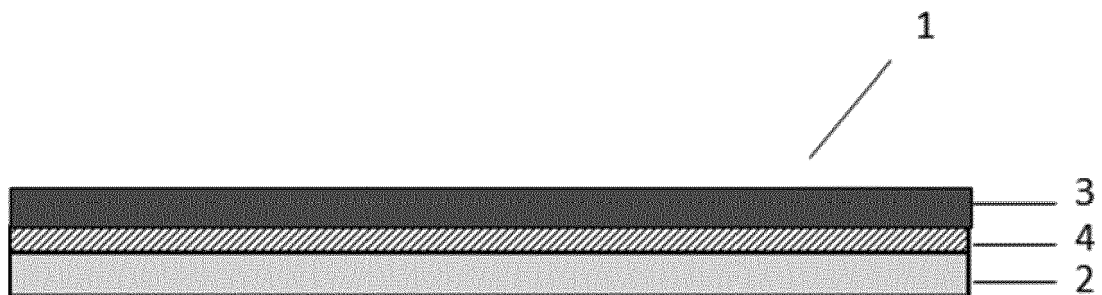


Fig. 2

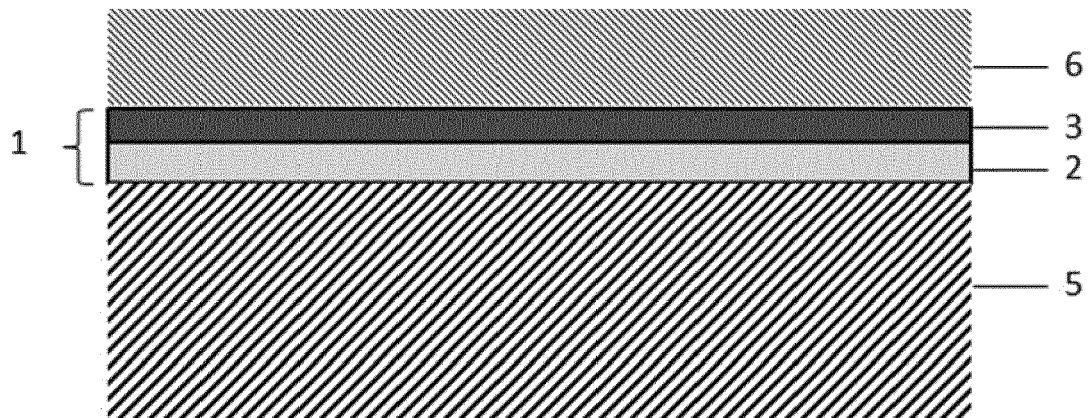


Fig. 3



EUROPEAN SEARCH REPORT

Application Number
EP 18 16 4382

5

10

15

20

25

30

35

40

45

50

55

1

EPO FORM 1503 03.82 (P04C01)

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y	US 2015/231863 A1 (KNEBEL GUSTL [CH] ET AL) 20 August 2015 (2015-08-20) * claims 1,4,17,28,29 *	1-17	INV. C09J7/22 B32B13/12
Y	US 2015/291839 A1 (O'CONNOR IAN MICHAEL [US]) 15 October 2015 (2015-10-15) * claims 1,2,17 *	1-17	
			TECHNICAL FIELDS SEARCHED (IPC)
			E04D C08J C09J B32B
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 27 August 2018	Examiner Niaounakis, Michael
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 18 16 4382

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

27-08-2018

10

15

20

25

30

35

40

45

50

55

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2015231863 A1	20-08-2015	CN 104583351 A	29-04-2015
		EP 2885361 A1	24-06-2015
		US 2015231863 A1	20-08-2015
		WO 2014029763 A1	27-02-2014

US 2015291839 A1	15-10-2015	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 8793862 B2 [0006]
- US 20150231863 A1 [0007]
- WO 2014187865 A1 [0051]
- WO 2015014725 A1 [0051]
- WO 2015014726 A1 [0051]
- WO 2016083310 A1 [0051]
- WO 2016083311 A1 [0051]
- WO 2016083312 A1 [0051]
- WO 2016083309 A1 [0051]
- US 3971751 A [0080]
- US 6207766 B [0080]