

Description**Field of the invention**

5 This invention relates to a primer composition for application to a substrate to promote adhesion of a room-temperature-vulcanisable (RTV) silicone rubber coating.

RTV silicone rubber coatings are applied to underwater surfaces, for example ships' hulls, the cooling water inlets and outlets of power stations, fish-farming equipment and the underwater and splash-zone surfaces of oil production platforms, to inhibit fouling by aquatic organisms such as algae and barnacles.

Background of the invention

15 Silicone rubber fouling-resistant coatings are described for example in GB-A-1307001, GB-A-1470465, GB-A-1581727, GB-A-2141436, EP-A-16195 and US-A-3702778. RTV silicone rubber coatings have also been suggested as coatings inhibiting the adhesion of ice, for example on the superstructure and topsides of ships.

A problem in the use of such RTV silicone rubber coatings is that it is difficult to make them adhere well to substrates. This problem is discussed in EP-A-16195 which proposes applying the RTV silicone rubber as a cladding on a fabric backing.

20 Various primer compositions have been suggested for room-temperature-vulcanisable silicone rubber antifoulings. US-A-3702778 proposes a crosslinkable silicone paste. EP-A-89066 proposes a mixture of an epoxysilane and a silane containing an unsaturated hydrocarbon group. JP-A-53-137231, JP-A-53-137233 and JP-A-53-137234 propose various elastomeric materials such as polyurethane, natural rubber, chloroprene or neoprene rubber or butyral/silicone rubber. EP-A-323906 and EP-A-329375 propose a silicone resin containing an aminosilane.

25 US-A-4070421 describes the use of chlorinated polyethylene as a primer for improving adhesion of coatings on polyolefin surfaces.

Summary of the invention

30 A primer composition according to the invention for application to a substrate to promote adhesion of an RTV silicone rubber coating comprises:

(A) an aminosilane material which is

(i) a primary amine-functional silane of the formula:



where the radicals R, which can be the same or different, are monovalent hydrocarbon radicals having 1 to 12 carbon atoms and optionally containing an ether linkage; R¹ is an alkylene radical having 2 to 4 carbon atoms or a divalent aliphatic ether radical having 3 to 8 carbon atoms; R² is hydrogen or an alkylene radical of 2 to 4 carbon atoms tipped with a primary amine group; and x is 2 or 3; or

40 (ii) the reaction product of a primary amine-functional silane of the formula (I) with an epoxy-functional silane of the formula:



where A is an epoxide-substituted monovalent hydrocarbon radical having 4 to 12 carbon atoms; the radicals B, which can be the same or different, are alkyl radicals having 1 to 4 carbon atoms; and a is 0 or 1; or

45 (iii) the reaction product of a primary amine-functional silane of the formula (I) with an alpha, omega-dihydroxypolydimethylsiloxane oil of the formula:



in which y is 2 to 60;

50 (B) a chlorinated polyolefin; and

(C) a room-temperature-curable polydiorganosiloxane.

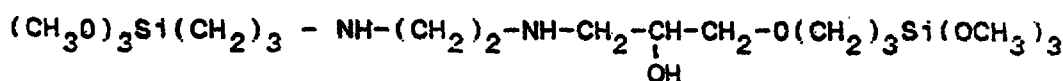
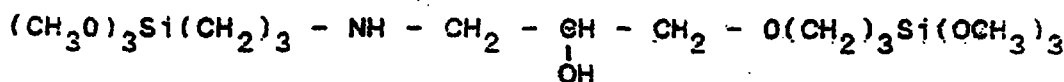
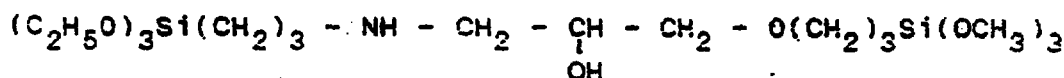
Detailed disclosure

55 In the primary amine-functional silane of formula (I) the radicals R are preferably alkyl, for example methyl, ethyl, hexyl or octyl, aryl, for example phenyl, or aralkyl, for example benzyl. The alkylene radical R¹ is preferably $-(CH_2)_3-$, $-(CH_2)_4-$ or methyl-substituted trimethylene, or can be $-(CH_2)_3-O-(CH_2)_2-$, $-(CH_2)_3-O-(CH_2)_3-$ or $-CH_2-O-(CH_2)_2-$. R² is preferably hydrogen or $-CH_2CH_2NH_2$. It may be preferred to separate any ether oxygen

atom in R and R¹ by at least two carbon atoms from the nearest heteroatom. Examples of primary amine-functional silanes of formula (I) are:

(CH₃O)₃Si(CH₂)₃NH(CH₂)₂NH₂; (CH₃CH₂OCH₂CH₂O)₃Si(CH₂)₂NH₂; (C₂H₅O)₃Si(CH₂)₃NH₂; (CH₃OCH₂CH₂O)₃Si(CH₂)₃NH₂; (C₂H₅O)₃Si(CH₂)₃O(CH₂)₃NH₂; (C₂H₅O)₂C₆H₅Si(CH₂)₃NH₂; (C₂H₅O)₃SiCH₂O(CH₂)₂NH₂; (C₂H₅O)₃Si(CH₂)₃O(CH₂)₂NH₂; and (C₂H₅O)₂CH₃Si(CH₂)₃NH₂. Mixtures of two or more primary amine-functional silanes (I) may be used if desired.

The primary amine-functional silane (I) is preferably used as such in the primer composition. It can however be replaced wholly or in part by a reaction product of the primary amine-functional silane (I) and an epoxy-functional silane (II). The group A in the epoxy-functional silane (II) is preferably a glycidioxy-substituted alkyl group, for example 3-glycidioxypropyl. The epoxy-functional silane (II) can for example be 3-glycidioxypropyl trimethoxy silane, 3-glycidioxypropyl diethoxy methoxy silane, 2-glycidioxypropyl trimethoxy silane, 3-(3,4-epoxycyclohexyl)propyl trimethoxy silane or 2-(3,4-epoxy-4-methylcyclohexyl)-ethyl trimethoxy silane. Examples of preferred reaction products of an amine-functional silane (I) and an epoxy-functional silane (II) are:



The aminosilane (I) and the epoxysilane (II) can be reacted at 20-80°C, preferably using 0.4-1.2 primary amine groups of aminosilane (I) per epoxide group in (II).

In a further alternative, the primary amine-functional silane (I) is replaced wholly or in part by a reaction product of the primary amine-functional silane (I) and an alpha, omega-dihydroxypolydimethylsiloxane (III). (I) and (III) can be reacted at 20-80°C, preferably using 0.4-1.2 alkoxy groups of aminosilane (I) per silanol group in (III).

The chlorinated polyolefin (B) preferably has a molecular weight of 5,000 to 50,000 and a chlorine content of 15 to 75%, most preferably 17 to 40%, by weight. Chlorinated polyolefins are commercially available. They can be prepared by treating a polyolefin with chlorine in the presence of a peroxide catalyst. The chlorination reaction is preferably carried out in a solvent for the polyolefin starting material. The polyolefin is preferably a poly(alpha-olefin) such as polyethylene or polypropylene. The polyolefin can be of high or low density, amorphous or crystalline. It can be a copolymer of two or more olefins, preferably alpha-olefins. Suitable chlorinated polyolefins are described for example in US-A-3561965 and US-A-4070421.

The chlorinated polyolefin (B) can be used in conjunction with another chlorinated hydrocarbon resin, for example a chlorinated polyterpene resin or chlorinated polystyrene. The polystyrene is preferably of low molecular weight (less than 5000). Such a chlorinated hydrocarbon resin preferably has a similar degree of chlorination to the chlorinated polyolefin. The chlorinated hydrocarbon resin can for example be used in an amount of from 1 to 100% by weight based on the chlorinated polyolefin (B).

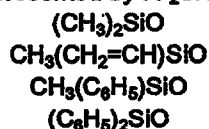
The aminosilane material (A) is generally used at 0.1 to 50% by weight based on the chlorinated material (chlorinated polyolefin (B) plus any other chlorinated hydrocarbon resin), most preferably 1 to 20% by weight.

The room-temperature-curable polydiorganosiloxane (C) is preferably a polydiorganosiloxane of viscosity 700 to 1,000,000 mPa s at 25°C. It preferably contains silicon-bonded hydroxyl groups, for example an alpha,omega-dihydroxypolydiorganosiloxane, or silicon-bonded hydrolysable groups, for example a polydiorganosiloxane tipped with silicon-bonded hydrolysable groups. More preferably, it is formed of recurring diorganosiloxy units of the formula -R⁴₂SiO- where the radicals R⁴, which can be the same or different, represent hydrocarbon radicals having 1 to 10 carbon atoms. It is preferred that at least 50% of the radicals R⁴ are methyl

groups. The dihydroxypolydiorganosiloxane may further contain monoorganosiloxy groups of the formula $R^4SiO_{1.5}$ and/or siloxy groups of the formula SiO_2 in a maximum proportion of 2% with respect to the number of diorganosiloxy groups R^4_2SiO .

The hydrocarbon radicals represented by the symbol R^4 in the di- and mono-organosiloxy units may suitably be selected from alkyl radicals such as methyl, ethyl, n-propyl, isopropyl, n-butyl, n-pentyl, n-hexyl, 2-ethyl hexyl or n-octyl, cycloalkyl radicals having from 4 to 8 carbon atoms such as cyclopentyl, cyclohexyl or methylcyclohexyl, alkenyl radicals having from 2 to 4 carbon atoms such as vinyl, allyl or buten-2-yl, and aryl radicals having from 6 to 8 carbon atoms such as phenyl, tolyl or xylyl.

As preferred examples of the groups represented by R^4_2SiO the following formulae are noted:



One example of a suitable alpha, omega-dihydroxy polydimethylsiloxane is that sold by Rhone Poulenc under the trade name "48V 3500".

Alpha, omega-dihydroxypolydiorganosiloxanes can readily be prepared by well-known techniques described, for example, in FR-A-1134005, FR-A-1198749 and FR-A-1226745. The polydiorganosiloxanes are preferably separated from volatile by-products before use, for example by the devolatilisation process described in US-A-4356116.

Preferred alpha, omega-dihydroxypolydimethylsiloxanes consist of successive groups of the formula $(CH_3)_2SiO$ or contain up to 10%, for example 2-10%, by mole of their groups R^4 as phenyl groups, for example in the form of $(C_6H_5)_2SiO$ units.

Alpha, omega-dihydroxypolydiorganosiloxanes are generally used with a curing agent, for example a compound containing at least two silicon-bonded hydrolysable groups per molecule. Examples of suitable curing agents are ketiminoxysilanes, acyloxysilanes and alkoxysilanes. tetraalkyl titanates and aluminium alcoholates.

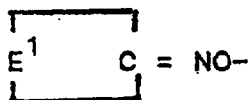
A ketiminoxysilane curing agent preferably contains at least two silicon-bonded hydrolysable ketiminoxy groups per molecule. Such a curing agent is preferably used at 1 to 18 parts by weight per 100 parts of alpha, omega-dihydroxy- polydiorganosiloxane. The ketiminoxysilane curing agent may have the general formula:



in which:

Y^1 represents a hydrocarbon radical having 1 to 10 carbon atoms, which may be substituted by halogen or cyano;

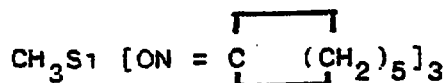
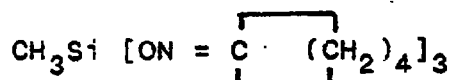
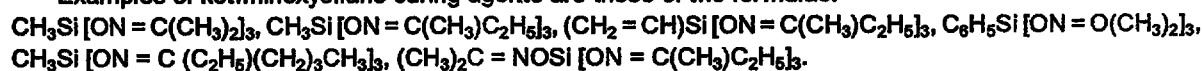
Z^1 represents a hydrolysable radical of the formula: $(Z^2)_2C = NO-$ or



in which the groups Z^2 , which can be the same or different, represent C_1 - C_8 hydrocarbon radicals and E^1 represents a C_4 - C_8 alkylene radical; the groups Z^1 can be the same or different; and r represents 0 or 1.

Examples of group Y^1 are those listed above as examples of group R^4 in the diorganosiloxy units.

Examples of ketiminoxysilane curing agents are those of the formulae:

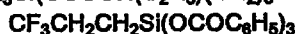
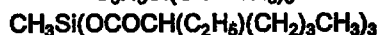


$\text{Si}[\text{ON} = \text{C}(\text{C}_2\text{H}_5)(\text{CH}_3)_2]_4$ or $\text{Si}[\text{ON} = \text{C}(\text{CH}_3)_2]_4$ and their mixtures.

An acyloxysilane curing agent can for example have the formula:



where R^5 is defined as for group R^4 mentioned above, R^6 is a monovalent hydrocarbon radical, e.g. of up to 8 carbon atoms, without aliphatic unsaturation and a is 0 or 1. The radicals R^6 can for example be alkyl such as methyl, ethyl, n-propyl, n-butyl or n-hexyl, cycloalkyl such as cyclopentyl or cyclohexyl, or aryl such as phenyl, tolyl or xylyl. Examples of acyloxysilane curing agents are:

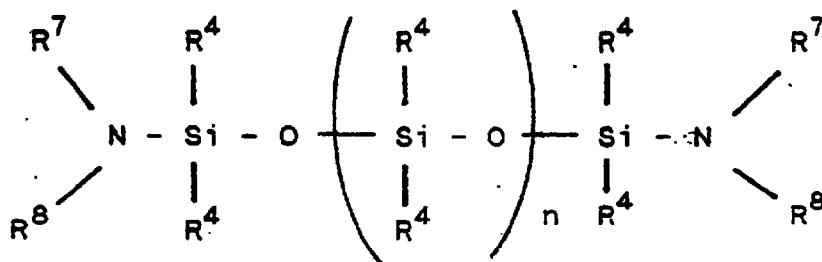


An acyloxysilane curing agent can for example be used at 2-20 % by weight based on the alpha, omega-dihydroxypolydiorganosiloxane.

An alkoxysilane curing agent can for example be a tetraalkyl orthosilicate (tetraalkoxysilane) such as tetraethyl orthosilicate or an alkyl trialkoxysilane such as methyl trimethoxysilane, ethyl trimethoxysilane or methyl triethoxysilane. Alkoxysilane curing agents such as tetraethyl orthosilicate are particularly preferred for use with moisture-curable polydiorganosiloxanes.

The room-temperature-curable polydiorganosiloxane (C) can be moisture-curable because atmospheric moisture is usually present when coating a marine surface. A moisture-curable polydiorganosiloxane can for example have hydrolysable end groups. The polydiorganosiloxane (C) containing silicon-bonded hydrolysable groups is preferably formed by combining an alpha,omega-dihydroxypolydiorganosiloxane with a compound containing at least two silicon-bonded hydrolysable groups per molecule. Examples of suitable compounds of this type are the ketiminoxysilanes and acyloxysilanes described above as curing agents, for example methyl triacetoxysilane, which form polydiorganosiloxanes tipped with silicon-bonded hydrolysable ketiminoxy or acyloxy groups. Reaction between the silicon-bonded hydroxyl groups of the alpha,omega-dihydroxypolydiorganosiloxane and the silicon-bonded hydrolysable groups of the said compound generally takes place as these materials are combined, so that the polydiorganosiloxane (C) is at least partially tipped with silicon-bonded hydroxyl groups.

An alternative polydiorganosiloxane (C) tipped with silicon-bonded hydrolysable groups is an amine-tipped polydiorganosiloxane, for example an alpha,omega-diaminopolydiorganosiloxane of the formula:



where R^4 is defined as above, n is an integer such that the polydiorganosiloxane has a viscosity of 700-1,000,000 mPa s at 25°C, and R^7 and R^8 each represent hydrogen or a monovalent hydrocarbon group having 1 to 10 carbon atoms. Most preferably R^7 represents hydrogen and R^8 represents an alkyl group having 2 to 6 carbon atoms, for example ethyl, propyl, isopropyl, n-butyl or sec-butyl (but-2-yl). Examples of amine-tipped polydiorganosiloxanes are sold under the Trade Marks "Silgan 500" and "Silgan 501J".

The room-temperature-curable polydiorganosiloxane (C) is preferably used at 0.1 to 100 parts by weight, more preferably 1 to 50 parts by weight, per part by weight of the chlorinated material (chlorinated polyolefin (B) plus any other chlorinated hydrocarbon resin).

The primer composition may contain a catalyst for the room-temperature curing of the polydiorganosiloxane. Examples of catalysts are metallic and organometallic salts of carboxylic acids. Metallic salts may be salts of tin, lead, nickel, cobalt, iron, chromium, zinc or manganese, for example stannous octoate. Preferred organometallic salts are diorganotin carboxylate compounds such as dibutyltin dilaurate or dibutyltin acetate. Organic titanium derivatives containing at least one -Ti-O-Si- or -Ti-O-C- linkage, e.g. an alkanolamine titanate, and organic zirconium derivatives can be used as catalyst, as described in US-A-4525565.

The primer compositions preferably contain an organic diluent which can for example be an aliphatic, cy-

5 cloaliphatic or aromatic hydrocarbon which is optionally halogenated such as n-heptane, n-octane, cyclohexane, methylcyclohexane, toluene, xylene, mesitylene, cumene, tetrahydronaphthalene, perchloroethylene, trichloroethane, tetrachloroethane, chlorobenzene or orthodichlorobenzene, an aliphatic or cycloaliphatic ketone such as methylethylketone, methylisobutylketone, methylisoamylketone, cyclohexanone or isophorone; an ether such as a dialkyl ether of ethylene glycol or propylene glycol, or an ester such as ethyl acetate, butyl acetate or ethoxyethyl acetate. The diluent is preferably a solvent for the chlorinated polyolefin (B), including any other chlorinated hydrocarbon resin present. The weight ratio of diluent to chlorinated polyolefin plus any other chlorinated hydrocarbon resin is preferably in the range 1:3 to 20:1, more preferably 2:3 to 10:1. The weight ratio of diluent to room-temperature-curable polydiorganosiloxane is usually 1:50 to 20:1, preferably 1:10 to 3:1.

15 The primer composition can be prepared by mixing the aminosilane material (A) and the chlorinated-polyolefin (B) with the room-temperature-curable polydiorganosiloxane (C). The chlorinated polyolefin (B) and any other chlorinated hydrocarbon resin present are preferably dissolved in an organic solvent before mixing with the aminosilane material (A) and the polydiorganosiloxane (C).

20 The primer composition can also contain additives selected from pigments, mineral fillers, thixotropic agents, stabilisers, surfactants, antioxidants and plasticisers. It may be preferred to include colouring pigments in the primer composition so that it can be overcoated by a fouling-resistant layer of clear RTV silicone rubber. When incorporating pigments, it may be necessary to take precautionary steps to avoid any moisture present in the pigment from instigating premature curing of the room-temperature-curable polydiorganosiloxane (C). The simplest precaution is to ensure that any pigments used are thoroughly dry. Alternatively, the pigments can be dispersed in a diluent, preferably a polydiorganosiloxane, which inhibits reaction of any moisture present in the pigment with the room-temperature-curable polydiorganosiloxane (C). The pigment can for example be dispersed in a non-reactive polydiorganosiloxane oil such as a methyltipped polydimethylsiloxane oil before the pigment contacts the room-temperature-curable polydiorganosiloxane (C) (including any curing agent therefor) and preferably also before the pigment contacts the aminosilane material (A). In an alternative procedure the pigment is dispersed in a liquid hydroxyl-tipped polydiorganosiloxane before the pigment contacts the aminosilane material (A) or any curing agent or material containing silicon-bonded hydrolysable groups which forms part of the room-temperature-curable polydiorganosiloxane (C). When this alternative procedure is used, the liquid hydroxyl-tipped polydiorganosiloxane used as dispersion medium will generally become co-cured with the room-temperature-curable polydiorganosiloxane (C). It can itself be used as the room-temperature-curable polydiorganosiloxane (C), in conjunction with a curing agent added later. It is generally preferred however that a liquid hydroxyl-tipped polydiorganosiloxane used as dispersion medium for the pigment forms only part of the polydiorganosiloxane (C); for example it can be used with a later-added moisture-curable polydiorganosiloxane (C) tipped with hydrolysable groups.

35 The primer composition is particularly effective in promoting adhesion to organic resin substrates such as neoprene rubber, chlorinated rubber, block copolymer rubbers such as polystyrene/polybutadiene or polystyrene/poly(ethylene-butylene) rubbers, polyurethanes, (both elastomers and thermoplastic resins), epoxy coatings, vinyl resins such as vinyl chloride polymers or alkyd resins. These resins may for example be in the form of cladding in the case of neoprene and similar rubbers, or may be previously-applied coatings, for example anticorrosive coatings which are to be covered by a silicone rubber antifouling paint, or old antifouling coatings which are to be overcoated. The primer composition also promotes adhesion to metal substrates such as aluminium or steel.

45 The primer composition can be applied to the substrate by any known coating technique. Usually it is applied by spray, brush or roller.

50 The RTV silicone rubber fouling-resistant coating which is applied over the primer composition can for example be based on an alpha, omega-dihydroxypolydiorganosiloxane as described above, used with a curing agent selected from those described above and optionally a catalyst selected from those described above. Alternatively, the RTV silicone rubber can be a polydiorganosiloxane tipped with silicon-bonded hydrolysable groups as described above, for example silicon-bonded ketiminoxy or acyloxy groups. It may be preferred that the curing agent or silicon-bonded hydrolysable groups in the room-temperaturecurable diorganopolysiloxane (C) in the primer composition and the curing agent or silicon-bonded hydrolysable groups in the RTV silicone rubber coating are the same. The RTV silicone rubber coating preferably includes a non-reactive silicone oil, for example of the formula: $Q_3Si-O-(SiQ_2-O)_nSiQ_3$, wherein each group Q represents a hydrocarbon radical having 1-10 carbon atoms and n is an integer such that the silicone oil has a viscosity of 20 to 5000 m Pa s. At least 10% of the groups Q are generally methyl groups and at least 2% of the groups Q are preferably phenyl groups. Most preferably, at least 25% of the $-SiQ_2-O-$ units are methylphenylsiloxane units. Most preferably the non-reactive silicone oil is a methyl-terminated poly(-methylphenylsiloxane). The oil preferably has a viscosity of 20 to 1000 m Pa s and is preferably used at 1 to 50%, most preferably 2 to 20%, by weight based on

the RTV silicone rubber. An example of a preferred non-reactive silicone oil is that sold under the Trade Mark "Rhodorsil Huile 550". The non-irreactive silicone oil improves the resistance of the composition to aquatic fouling.

5 Instead of, or in addition to, the non-reactive silicone oil, the RTV silicone rubber composition can contain a non-reactive fluid organic hydrocarbon, for example a lubricating mineral oil such as white oil, a low molecular weight polybutene or petrolatum or a liquid paraffin/petrolatum mixture. Such a non-reactive fluid organic hydrocarbon is preferably absent from the primer composition.

10 The primer composition improves the overall adhesion of the RTV silicone rubber to the substrate to a greater extent than can be achieved in the absence of any of the essential components (A) and (B). The aminosilane material (A) and chlorinated polyolefin (B) ensure strong adhesion of the primer to the RTV silicone rubber and to the organic resin substrate respectively. We have however found that when a composition comprising aminosilane material (A), chlorinated polyolefin (B) and solvent is applied to many organic resin substrates it is rapidly absorbed by the substrate, so that adhesion of a subsequently applied RTV silicone rubber
15 coating is poor unless it is applied very soon. The room-temperature-curable polydiorganosiloxane (C) counteracts the tendency for the primer composition to be absorbed by the substrate, allowing a much longer time period, for example up to a week or even longer, within which overcoating with an RTV silicone rubber composition can be achieved with good adhesion.

20 The primer composition according to the invention has much greater adhesion to many substrates, in particular neoprene, chloroprene or hydrocarbon rubbers, than a composition which does not contain chlorinated polyolefin. On all substrates, including those such as epoxy resin where the simple combination of room-temperature-curable polydiorganosiloxane and aminosilane material gives good adhesion, the chlorinated polyolefin improves the resistance to sea water immersion; good adhesion of the primer composition to the substrate and of the RTV silicone rubber top coat to the primer composition is maintained even after 18 months
25 or more of immersion in sea water.

The invention is illustrated by the following Examples in which parts and percentages are by weight.

Example 1

30 25 parts of a 40% solution in xylene of a chlorinated polyethylene (chlorine content 22%) was mixed with 2 parts N-(2-aminoethyl)-3-aminopropyl trimethoxy silane and diluted with 73 parts xylene.

14 parts of the resulting composition was mixed with 61 parts of a room-temperature-curable polydiorganosiloxane composition and 25 parts methyl isoamyl ketone solvent. The room-temperature-curable polydiorganosiloxane composition comprised an alpha, omega-dihydroxypolydimethylsiloxane used with a keti-
35 minoxysilane curing agent.

The resulting primer composition was applied to a neoprene rubber substrate, and also to substrates coated with epoxy resin, polyurethane, vinyl resin and alkyd resin anticorrosive paints, and to a substrate having the residue of an old antifouling paint based on rosin, a vinyl chloride copolymer and cuprous oxide. In all cases the coating of primer composition could be overcoated with an RTV silicone rubber fouling-resistant composition based on an alpha, omega-dihydroxypolydiorganosiloxane with a ketiminoxysilane curing agent and a
40 non-reactive poly-(methyl phenyl siloxane) oil about 10 minutes after application of the primer composition with good adhesion of the RTV composition, and could also be overcoated with the RTV composition 24 hours later with good adhesion.

45 The overcoated materials were immersed in sea water. Adhesion between the primer composition and the substrates, and between the RTV silicone rubber fouling-resistant coating and the primer composition, remained strong after 18 months immersion in sea water.

Example 2

50 29.7 parts of pigments and fillers (barytes, titanium dioxide, fumed silica and black iron oxide) and 0.1 part of dibutyltin dilaurate curing catalyst were dispersed by milling in 6.7 parts of non-reactive methyl-tipped polydimethylsiloxane oil and 10.6 parts of methyl isoamyl ketone solvent. The resulting pigment dispersion was mixed with 36.4 parts of room-temperature-curable polydimethylsiloxane tipped with ketiminox groups, 8.3 parts of the solution of chlorinated polyethylene and N-(2-aminoethyl)-3-aminopropyl trimethoxy silane described in Example 1 and 8.2 parts of methyl isoamyl ketone.
55

The resulting primer composition was applied to epoxy resin, neoprene rubber and urethane rubber substrates. These samples were overcoated after 16 to 48 hours with the RTV silicone rubber of Example 1.

The overcoated materials were immersed in sea water. Adhesion between the primer composition and the substrates, and between the RTV silicone rubber fouling-resistant coating and the primer composition,

remained strong after 16 months' immersion in sea water.

Example 3

28.1 parts of pigments and fillers (titanium dioxide, barytes, black iron oxide and fumed silica) were dispersed by milling in 11.5 parts of liquid hydroxyl-tipped polydimethylsiloxane with 0.5 part of wetting aid and 11.4 parts of methyl isoamyl ketone. The resulting pigment dispersion was mixed with 7.6 parts of the solution of chlorinated polyethylene and N-(2-aminoethyl)-3-aminopropyl trimethoxy silane described in Example 1, 30.9 parts of room-temperature-curable polydimethylsiloxane tipped with ketiminoxy groups, 0.03 part of dibutyltin dilaurate and 10.0 parts of methyl isoamyl ketone.

The resulting primer composition was applied to substrates of epoxy resin, aluminium, urethane rubber, neoprene rubber, a substrate having a residue of old antifouling paint as described in Example 1, polystyrene/polybutadiene block copolymer rubber and polystyrene/poly(ethylene-butylene) block copolymer rubber. These samples were overcoated after 16 to 48 hours with the RTV silicone rubber of Example 1.

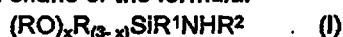
The overcoated materials were immersed in sea water. Adhesion between the primer composition and the substrates, and between the RTV silicone rubber fouling-resistant coating and the primer composition, remained strong after 6 months' immersion in sea water.

Claims

1. A primer composition for application to a substrate to promote adhesion of a room-temperature-vulcanisable silicone rubber-coating, which primer composition comprises:

(A) an aminosilane material which is

(i) a primary amine-functional silane of the formula:

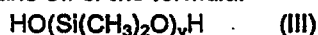


where the radicals R, which can be the same or different, are monovalent hydrocarbon radicals having 1 to 12 carbon atoms and optionally containing an ether linkage; R¹ is an alkylene radical having 2 to 4 carbon atoms or a divalent aliphatic ether radical having 3 to 8 carbon atoms; R² is hydrogen or an alkylene radical of 2 to 4 carbon atoms tipped with a primary amino group; and x is 2 or 3; or (ii) the reaction product of a primary amine-functional silane of the formula (I) with an epoxy-functional silane of the formula:



where A is an epoxide-substituted monovalent hydrocarbon radical having 4 to 12 carbon atoms; the radicals B, which can be the same or different, are alkyl radicals having 1 to 4 carbon atoms; and a is 0 or 1; or

(iii) the reaction product of a primary amine-functional silane of the formula (I) with an alpha, omega-dihydroxypolydimethylsiloxane oil of the formula:



in which y is 2 to 60;

(B) a chlorinated polyolefin; and

(C) a room-temperature-curable polydiorganosiloxane.

2. A primer composition according to claim 1, characterised in that the room-temperature-curable polydiorganosiloxane (C) is an alpha, omega-dihydroxypolydiorganosiloxane used in conjunction with a ketiminoxysilane curing agent.
3. A primer composition according to claim 1, characterised in that the room-temperature-curable polydiorganosiloxane (C) is an alpha, omega-dihydroxypolydiorganosiloxane used in conjunction with an acyloxysilane curing agent.
4. A primer composition according to claim 1, characterised in that the room-temperature-curable polydiorganosiloxane (C) is an alpha, omega-dihydroxypolydiorganosiloxane used in conjunction with an alkoxysilane curing agent.
5. A primer composition according to claim 1, characterised in that the room-temperature-curable polydiorganosiloxane (C) is a polydiorganosiloxane tipped with silicon-bonded hydrolysable groups.



remained strong after 16 months' immersion in sea water.

Example 3

28.1 parts of pigments and fillers (titanium dioxide, barytes, black iron oxide and fumed silica) were dispersed by milling in 11.5 parts of liquid hydroxyl-tipped polydimethylsiloxane with 0.5 part of wetting aid and 11.4 parts of methyl isoamyl ketone. The resulting pigment dispersion was mixed with 7.6 parts of the solution of chlorinated polyethylene and N-(2-aminoethyl)-3-aminopropyl trimethoxy silane described in Example 1, 30.9 parts of room-temperature-curable polydimethylsiloxane tipped with ketiminoxy groups, 0.03 part of dibutyltin dilaurate and 10.0 parts of methyl isoamyl ketone.

The resulting primer composition was applied to substrates of epoxy resin, aluminium, urethane rubber, neoprene rubber, a substrate having a residue of old antifouling paint as described in Example 1, polystyrene/polybutadiene block copolymer rubber and polystyrene/poly(ethylene-butylene) block copolymer rubber. These samples were overcoated after 16 to 48 hours with the RTV silicone rubber of Example 1.

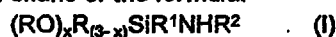
The overcoated materials were immersed in sea water. Adhesion between the primer composition and the substrates, and between the RTV silicone rubber fouling-resistant coating and the primer composition, remained strong after 6 months' immersion in sea water.

Claims

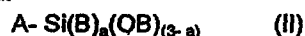
1. A primer composition for application to a substrate to promote adhesion of a room-temperature-vulcanisable silicone rubber-coating, which primer composition comprises:

(A) an aminosilane material which is

(i) a primary amine-functional silane of the formula:

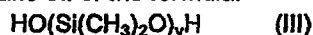


where the radicals R, which can be the same or different, are monovalent hydrocarbon radicals having 1 to 12 carbon atoms and optionally containing an ether linkage; R¹ is an alkylene radical having 2 to 4 carbon atoms or a divalent aliphatic ether radical having 3 to 8 carbon atoms; R² is hydrogen or an alkylene radical of 2 to 4 carbon atoms tipped with a primary amino group; and x is 2 or 3; or (ii) the reaction product of a primary amine-functional silane of the formula (I) with an epoxy-functional silane of the formula:



where A is an epoxide-substituted monovalent hydrocarbon radical having 4 to 12 carbon atoms; the radicals B, which can be the same or different, are alkyl radicals having 1 to 4 carbon atoms; and a is 0 or 1; or

(iii) the reaction product of a primary amine-functional silane of the formula (I) with an alpha, omega-dihydroxypolydimethylsiloxane oil of the formula:



in which y is 2 to 60;

(B) a chlorinated polyolefin; and

(C) a room-temperature-curable polydiorganosiloxane.

2. A primer composition according to claim 1, characterised in that the room-temperature-curable polydiorganosiloxane (C) is an alpha, omega-dihydroxypolydiorganosiloxane used in conjunction with a ketiminoxysilane curing agent.
3. A primer composition according to claim 1, characterised in that the room-temperature-curable polydiorganosiloxane (C) is an alpha, omega-dihydroxypolydiorganosiloxane used in conjunction with an acyloxysilane curing agent.
4. A primer composition according to claim 1, characterised in that the room-temperature-curable polydiorganosiloxane (C) is an alpha, omega-dihydroxypolydiorganosiloxane used in conjunction with an alkoxysilane curing agent.
5. A primer composition according to claim 1, characterised in that the room-temperature-curable polydiorganosiloxane (C) is a polydiorganosiloxane tipped with silicon-bonded hydrolysable groups.



6. A primer composition according to claim 5, characterised in that the silicon-bonded hydrolysable groups are ketiminoxy, acyloxy or amine groups.
7. A primer composition according to any of claims 1 to 6, characterised in that the chlorinated polyolefin (B) has a chlorine content of 17 to 40% by weight.
8. A primer composition according to any of claims 1 to 7, characterised in that the composition contains another chlorinated hydrocarbon resin in an amount of 1 to 100% by weight based on the chlorinated polyolefin (B).
9. A primer-composition according to any of claims 1 to 8, characterised in that the aminosilane material (A) is used at 1 to 20% by weight based on the weight of chlorinated polyolefin (B) plus any other chlorinated hydrocarbon resin present in the composition.
10. A primer composition according to any of claims 1 to 9, characterised in that the weight ratio of the room-temperature-curable polydiorganosiloxane (C) to the chlorinated polyolefin (B) plus any other chlorinated hydrocarbon resin present in the composition is 1:1 to 50:1.
11. A primer composition according to any of claims 1 to 10, characterised in that a pigment is dispersed in the composition.
12. A process for preparing a primer composition in which
 - (A) an aminosilane material which is
 - (i) a primary amine-functional silane of the formula:

$$(RO)_x R_{(3-x)} SiR^1 NHR^2 \quad (I)$$
 where the radicals R, which can be the same or different, are monovalent hydrocarbon radicals having 1 to 12 carbon atoms and optionally containing an ether linkage; R¹ is an alkylene radical having 2 to 4 carbon atoms or a divalent aliphatic ether radical having 3 to 8 carbon atoms; R² is hydrogen or an alkylene radical of 2 to 4 carbon atoms tipped with a primary amino group; and x is 2 or 3; or
 - (ii) the reaction product of a primary amine-functional silane of the formula (I) with an epoxy-functional silane of the formula:

$$A - Si(B)_a (OB)_{(3-a)} \quad (II)$$
 where A is an epoxide-substituted monovalent hydrocarbon radical having 4 to 12 carbon atoms; the radicals B, which can be the same or different, are alkyl radicals having 1 to 4 carbon atoms; and a is 0 or 1; or
 - (iii) the reaction product of a primary amine-functional silane of the formula (I) with an alpha, omega-dihydroxypolydimethylsiloxane oil of the formula:

$$HO(Si(CH_3)_2O)_yH \quad (III)$$
 in which y is 2 to 60;
 - and (B) a chlorinated polyolefin;
 - are mixed with
 - (C) a room-temperature-curable polydiorganosiloxane.
 13. A process according to claim 12, characterised in that a pigmented primer composition is prepared by dispersing a pigment in a non-reactive polydiorganosiloxane oil and mixing with the aminosilane material (A), the chlorinated polyolefin (B) and the room-temperature-curable polydiorganosiloxane (C), said step of dispersing the pigment in polydiorganosiloxane oil being carried out before the pigment contacts the aminosilane material (A) or the room-temperature-curable polydiorganosiloxane (C).
 14. A process according to claim 12, characterised in that a pigmented primer composition is prepared by dispersing a pigment in a liquid hydroxyl-tipped polydiorganosiloxane and mixing it with the aminosilane material (A), the chlorinated polyolefin (B) and the room-temperature-curable polydiorganosiloxane (C), said step of dispersing the pigment in a liquid polydiorganosiloxane being carried out before the pigment contacts the aminosilane material (A) or any curing agent or material containing silicon-bonded hydrolysable groups which forms part of the room-temperature-curable polydiorganosiloxane (C).
 15. A process according to claim 12, characterised in that a pigmented primer composition is formed by dispersing a pigment in a liquid hydroxyl-tipped polydiorganosiloxane and mixing it with the aminosilane material (A), the chlorinated polyolefin (B) and a curing agent which together with the liquid hydroxyl-tipped



polydiorganosiloxane forms the room-temperature-curable polydiorganosiloxane (C), said step of dispersing the pigment in a liquid polydiorganosiloxane being carried out before the pigment contacts the aminosilane material (A) or the said curing agent.

16. A process for coating a substrate with a room-temperature-vulcanisable silicone rubber, characterised in that the substrate is coated with a primer composition according to any of claims 1 to 11 and the room-temperature-vulcanisable silicone rubber composition is applied over the said primer composition.
17. A process according to claim 16, characterised in that the primer composition is as defined in any of claims 2 to 4 and the room-temperature-vulcanisable silicone rubber composition comprises an alpha,omega-dihydroxypolydiorganosiloxane used in conjunction with a curing agent of the same type as is used in the primer composition.
18. A process according to claim 16, characterised in that the primer composition is as defined in claim 5 or claim 6 and the room-temperature-vulcanisable silicone rubber composition comprises a polydiorganosiloxane tipped with silicon-bonded hydrolysable groups of the same type as those in the room-temperature-curable polydiorganosiloxane (C).

Patentansprüche

1. Grundierzusammensetzung zum Auftragen auf ein Substrat zwecks Haftungsverbesserung einer bei Raumtemperatur vulkanisierbaren Beschichtung aus Silikongummi, bestehend aus:

(A) einem Material aus Aminosilan, bei dem es sich um

(i) ein aminfunktionelles primäres Silan der Formel:



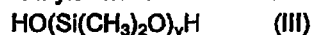
worin die Reste R, die gleich oder verschieden sein können, einwertige Kohlenwasserstoffreste mit 1 bis 12 Kohlenstoffatomen und gegebenenfalls einer Etherverknüpfung; R¹ einen Alkylrest mit 2 bis 4 Kohlenstoffatomen oder einen Zweiwertigen aliphatischen Etherrest mit 3 bis 8 Kohlenstoffatomen; R² Wasserstoff oder einen mit einer primären Aminogruppe terminierten Alkylrest mit 2 bis 4 Kohlenstoffatomen; und x 2 oder 3 bedeuten; oder

(ii) das Umsetzungsprodukt aus einem aminfunktionellen primären Silan der Formel (I) und einem epoxidfunktionellen Silan der Formel:



worin A ein durch Epoxid substituierter einwertiger Kohlenwasserstoffrest mit 4 bis 12 Kohlenstoffatomen; die Reste B, die gleich oder verschieden sein können, Alkylreste mit 1 bis 4 Kohlenstoffatomen; und a 0 oder 1 sind; oder

(iii) das Umsetzungsprodukt aus einem aminfunktionellen primären Silan der Formel (I) und einem alpha, omega-Dihydroxypolydimethylsiloxan-Öl der Formel:



handelt, worin y eine Zahl von 2 bis 60 bedeutet;

(B) einen chlorierten Polyolefin; und

(C) eine bei Raumtemperatur aushärtbaren Polydiorganosiloxan.

2. Grundierzusammensetzung nach Anspruch 1, dadurch gekennzeichnet, dass das bei Raumtemperatur aushärtbare Polydiorganosiloxan (C) ein in Verbindung mit einem Härter aus Ketiminoxysilan eingesetztes alpha, omega-Dihydroxypolydiorganosiloxan ist.
3. Grundierzusammensetzung nach Anspruch 1, dadurch gekennzeichnet, dass das bei Raumtemperatur aushärtbare Polydiorganosiloxan (C) ein in Verbindung mit einem Härter aus Acyloxysilan eingesetztes alpha, omega-Dihydroxypolydiorganosiloxan ist.
4. Grundierzusammensetzung nach Anspruch 1, dadurch gekennzeichnet, dass das bei Raumtemperatur aushärtbare Polydiorganosiloxan (C) ein in Verbindung mit einem Härter aus Alkoxysilan eingesetztes alpha, omega-Dihydroxypolydiorganosiloxan ist.
5. Grundierzusammensetzung nach Anspruch 1, dadurch gekennzeichnet, dass das bei Raumtemperatur aushärtbare Polydiorganosiloxan (C) ein mit siliciumgebundenen, hydrolysierbaren Gruppen terminiertes Polydiorganosiloxan ist.



6. Grundierzusammensetzung nach Anspruch 5, dadurch gekennzeichnet, das die siliciumgebundenen, hydrolysierbaren Gruppen Ketiminoxy-, Acyloxy- oder Amingruppen sind.
7. Grundierzusammensetzung nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß das chlorierte Polyolefin (B) einen Chlorgehalt von 17 bis 40 Gew.-% aufweist.
8. Grundierzusammensetzung nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, das die Zusammensetzung ein weiteres chloriertes Kohlenwasserstoffharz in einer Menge von 1 bis 100 Gew.-%, bezogen auf das chlorierte Polyolefin (B), enthält.
9. Grundierzusammensetzung nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß das Material aus Aminosilan (A) zu 1 bis 20 Gew.-%, bezogen auf das Gewicht an chloriertem Polyolefin (B) plus jedem weiteren in der Zusammensetzung enthaltenen chlorierten Kohlenwasserstoffharz, eingesetzt ist.
10. Grundierzusammensetzung nach einem der Ansprüche 1 bis 9, dadurch gekennzeichnet, daß das Gewichtsverhältnis von bei Raumtemperatur aushärtbarem Polydiorganosiloxan (C) zu dem chlorierten Polyolefin (B) plus jedem weiteren in der Zusammensetzung enthaltenen chlorierten Kohlenwasserstoffharz 1:1 bis 50:1 beträgt.
11. Grundierzusammensetzung nach einem der Ansprüche 1 bis 10, dadurch gekennzeichnet, daß in der Zusammensetzung ein Pigment dispergiert ist.
12. Verfahren zur Herstellung einer Grundierzusammensetzung, worin
 (A) ein Material aus Aminosilan, bei dem es sich um
 (i) ein aminfunktionelles primäres Silan der Formel:

$$(RO)_x R_{(3-x)} SiR^1 NHR^2 \quad (I)$$
 worin die Reste R, die gleich oder verschieden sein können, einwertige Kohlenwasserstoffreste mit 1 bis 12 Kohlenstoffatomen und gegebenenfalls einer Etherverknüpfung; R¹ einen Alkylrest mit 2 bis 4 Kohlenstoffatomen oder einen zweiwertigen aliphatischen Etherrest mit 3 bis 8 Kohlenstoffatomen; R² Wasserstoff oder einen mit einer primären Aminogruppe terminierten Alkylrest mit 2 bis 4 Kohlenstoffatomen; und x 2 oder 3 bedeuten; oder (ii) das Umsetzungsprodukt aus einem aminfunktionellen primären Silan der Formel (I) und einem epoxidfunktionellen Silan der Formel:

$$A-Si(B)_a(OB)_{(3-a)} \quad (II)$$
 worin A ein durch Epoxid substituierter einwertiger Kohlenwasserstoffrest mit 4 bis 12 Kohlenstoffatomen; die Reste B, die gleich oder verschieden sein können, Alkylreste mit 1 bis 4 Kohlenstoffatomen; und a 0 oder 1 sind; oder
 (iii) das Umsetzungsprodukt aus einem aminofunktionellen primären Silan der Formel (I) und einem alpha, omega-Dihydroxypolydimethylsiloxan-Öl der Formel:

$$HO(Si(CH_3)_2O)_yH \quad (III)$$
 handelt, worin y eine Zahl von 2 bis 60 bedeutet;
 und (B) ein chloriertes Polyolefin;
 mit
 (C) einem bei Raumtemperatur aushärtbaren Polydiorganosiloxan vermischt werden.
13. Verfahren nach Anspruch 12, dadurch gekennzeichnet, daß eine pigmentierte Grundierzusammensetzung durch Dispergieren eines Pigments in einem nichtreaktiven Polydiorganosiloxan-Öl und Vermischen mit dem Material aus Aminosilan (A), dem chlorierten Polyolefin (B) und dem bei Raumtemperatur aushärtbaren Polydiorganosiloxan (C) hergestellt wird; wobei das Dispergieren des Pigments in Polydiorganosiloxan-Öl vor der Kontaktierung des Pigments mit dem Material aus Aminosilan (A) oder dem bei Raumtemperatur aushärtbaren Polydiorganosiloxan (C) erfolgt.
14. Verfahren nach Anspruch 12, dadurch gekennzeichnet, das eine pigmentierte Grundierzusammensetzung durch Dispergieren eines Pigments in einem flüssigen, hydroxyterminierten Polydiorganosiloxan und Vermischen mit dem Material aus Aminosilan (A), dem chlorierten Polyolefin (B) und dem bei Raumtemperatur aushärtbaren Polydiorganosiloxan (C) hergestellt wird, wobei das Dispergieren des Pigments in einem flüssigen Polydiorganosiloxan vor der Kontaktierung des Pigments mit dem Material aus Aminosilan (A) oder irgendeinem Härter oder Material mit siliciumgebundenen, hydrolysierbaren Gruppen, das einen Bestandteil des bei Raumtemperatur aushärtbaren Polydiorganosiloxans (C) darstellt, erfolgt.



15. Verfahren nach Anspruch 12, dadurch gekennzeichnet, daß eine pigmentierte Grundierzusammensetzung durch Dispergieren eines Pigments in einem flüssigen, hydroxyterminierten Polydiorganosiloxan und Vermischen mit dem Material aus Aminosilan (A), dem chlorierten Polyolefin (B) und einem Härter, der zusammen mit dem flüssigen hydroxyterminierten Polydiorganosiloxan das bei Raumtemperatur aushärtbare Polydiorganosiloxan (C) bildet, hergestellt wird, wobei das Dispergieren des Pigments in einem flüssigen Polydiorganosiloxan vor der Kontaktierung des Pigments mit dem Material aus Aminosilan (A) oder jenem Härter erfolgt.
16. Verfahren zur Beschichtung eines Schichtträgers mit einem kaltvulkanisierbaren Silikongummi, dadurch gekennzeichnet, daß das Substrat mit einer Grundierzusammensetzung nach einem der Ansprüche 1 bis 11 beschichtet wird und die kaltvulkanisierbare Zusammensetzung aus Silikongummi über die Grundierzusammensetzung aufgetragen wird.
17. Verfahren nach Anspruch 16, dadurch gekennzeichnet, daß die Grundierzusammensetzung der in einem der Ansprüche 2 bis 4 angegebenen Definition entspricht, und die bei Raumtemperatur vulkanisierbare Zusammensetzung aus Silikongummi aus in Verbindung mit einem Härter des bei der Grundierzusammensetzung verwendeten Typs eingesetztem alpha, omega-Dihydroxypolydiorganosiloxan besteht.
18. Verfahren nach Anspruch 16, dadurch gekennzeichnet, daß die Grundierzusammensetzung der in Anspruch 5 oder Anspruch 6 angegebenen Definition entspricht, und die bei Raumtemperatur vulkanisierbare Zusammensetzung aus Silikongummi aus einem Polydiorganosiloxan besteht, das mit siliciumgebundenen, hydrolysierbaren Gruppen desselben Typs wie bei dem bei Raumtemperatur aushärtbaren Polydiorganosiloxan (C) terminiert ist.

Revendications

1. Composition de primaire à appliquer sur un substrat pour favoriser l'adhérence d'un revêtement de caoutchouc silicone vulcanisable à la température ambiante, cette composition de primaire comprenant
- (A) un aminosilane qui est
- (i) un silane à fonction amine primaire de formule
- $$(RO)_x R_{(3-x)} SiR^1 NHR^2 \quad (I)$$
- dans laquelle les radicaux R, qui peuvent être identiques ou différents, sont des radicaux hydrocarbonés monovalents comportant 1 à 12 atomes de carbone et contenant éventuellement une liaison éther; R¹ est un radical alkylène comportant 2 à 4 atomes de carbone ou un radical éther aliphatique divalent comportant 3 à 8 atomes de carbone; R² est un hydrogène ou un radical alkylène de 2 à 4 atomes de carbone à extrémités bloquées par un groupe amino primaire; et x est 2 ou 3; ou
- (ii) le produit de réaction d'un silane à fonction amine primaire de formule (I) avec un silane à fonction époxy de formule
- $$A-Si(B)_a(OB)_{(3-a)} \quad (II)$$
- dans laquelle A est un radical hydrocarboné monovalent substitué par un époxyde, comportant 4 à 12 atomes de carbone; les radicaux B, qui peuvent être identiques ou différents, sont des radicaux alkyle comportant 1 à 4 atomes de carbone; et a est 0 ou 1; ou
- (iii) le produit de réaction d'un silane à fonction amine primaire de formule (I) avec une huile d'alpha, oméga-dihydroxypolydiméthylsiloxane de formule:
- $$HO(Si(CH_3)_2O)_yH \quad (III)$$
- dans laquelle y est 2 à 60;
- (B) une polyoléfine chlorée; et
- (C) un polydiorganosiloxane durcissable à la température ambiante.
2. Composition de primaire selon la revendication 1, caractérisée en ce que le polydiorganosiloxane (C) durcissable à la température ambiante est un alpha,oméga-dihydroxypolydiorganosiloxane utilisé en conjonction avec un agent durcisseur de type cétiminoxysilane.
3. Composition de primaire selon la revendication 1, caractérisée en ce que le polydiorganosiloxane (C) durcissable à la température ambiante est un alpha,oméga-dihydroxypolydiorganosiloxane utilisé en conjonction avec un agent durcisseur de type acyloxysilane.



4. Composition de primaire selon la revendication 1, caractérisée en ce que le polydiorganosiloxane (C) durcissable à la température ambiante est un alpha, omégadihydroxypolydiorganosiloxane utilisé en conjonction avec un agent durcisseur de type alcoxysilane.
5. Composition de primaire selon la revendication 1, caractérisée en ce que le polydiorganosiloxane (C) durcissable à la température ambiante est un polydiorganosiloxane à extrémités bloquées par des groupes hydrolysables liés à un silicium.
6. Composition de primaire selon la revendication 5, caractérisée en ce que les groupes hydrolysables liés à un silicium sont des groupes cétiminoxy, acyloxy ou amine.
7. Composition de primaire selon l'une quelconque des revendications 1 à 6, caractérisée en ce que la polyoléfine chlorée (B) possède une teneur en chlore de 17 à 40% en poids.
8. Composition de primaire selon l'une quelconque des revendications 1 à 7, caractérisée en ce que la composition contient une autre résine hydrocarbonée chlorée, en une quantité de 1 à 100% en poids par rapport à la polyoléfine chlorée (B).
9. Composition de primaire selon l'une quelconque des revendications 1 à 8, caractérisée en ce que l'aminosilane (A) est utilisé à raison de 1 à 20% en poids, par rapport au poids de la polyoléfine chlorée (B) plus toute résine hydrocarbonée chlorée éventuellement présente dans la composition.
10. Composition de primaire selon l'une quelconque des revendications 1 à 9, caractérisée en ce que le rapport pondéral du polydiorganosiloxane (C) durcissable à la température ambiante à la polyoléfine chlorée (B) plus toute résine hydrocarbonée chlorée éventuellement présente dans la composition est de 1 : 1 à 50 : 1.
11. Composition de primaire selon l'une quelconque des revendications 1 à 10, caractérisée en ce que l'on disperse un pigment dans la composition.
12. Procédé de préparation d'une composition de primaire, dans lequel on mélange
 - (A) un aminosilane qui est
 - (i) un silane à fonction amine primaire de formule:

$$(RO)_x R_{(3-x)} SiR^1 NHR^2 \quad (I)$$
 dans laquelle les radicaux R, qui peuvent être identiques ou différents, sont des radicaux hydrocarbonés monovalents comportant 1 à 12 atomes de carbone et contenant éventuellement une liaison éther; R¹ est un radical alkylène comportant 2 à 4 atomes de carbone ou un radical éther aliphatique divalent comportant 3 à 8 atomes de carbone; R² est un hydrogène ou un radical alkylène de 2 à 4 atomes de carbone à extrémités bloquées par un groupe amino primaire; et x est 2 ou 3; ou
 - (ii) le produit de réaction d'un silane à fonction amine primaire de formule (I) avec un silane à fonction époxy de formule

$$A-Si(B)_a(OH)_{(3-a)} \quad (II)$$
 dans laquelle A est un radical hydrocarboné monovalent substitué par un époxyde, comportant 4 à 12 atomes de carbone; les radicaux B, qui peuvent être identiques ou différents, sont des radicaux alkyle comportant 1 à 4 atomes de carbone; et a est 0 ou 1; ou
 - (iii) le produit de réaction d'un silane à fonction amine primaire de formule (I) avec une huile d'alpha, omégadihydroxypolydiméthylsiloxane de formule:

$$HO(Si(CH_3)_2O)_yH \quad (111)$$
 dans laquelle y est 2 à 60;
 - et (B) une polyoléfine chlorée; avec
 - (C) un polydiorganosiloxane durcissable à la température ambiante.
13. Procédé selon la revendication 12, caractérisé en ce que l'on prépare une composition de primaire pigmentée par dispersion d'un pigment dans une huile de polydiorganosiloxane non réactive et mélange avec l'aminosilane (A), la polyoléfine chlorée (B) et le polydiorganosiloxane (C) durcissable à la température ambiante, ladite étape de dispersion du pigment dans l'huile de polydiorganosiloxane étant réalisée avant que le pigment n'entre en contact avec l'aminosilane (A) ou avec le polydiorganosiloxane (C) dur-



cissable à la température ambiante.

- 5 14. Procédé selon la revendication 12, caractérisé en ce que l'on prépare une composition de primaire pigmentée par dispersion d'un pigment dans un polydiorganosiloxane liquide à extrémités bloquées par des groupes hydroxyle et mélange de ce dernier avec l'aminosilane (A), la polyoléfine chlorée (B) et le polydiorganosiloxane (C) durcissable à la température ambiante, ladite étape de dispersion du pigment dans le polydiorganosiloxane liquide étant réalisée avant que le pigment n'entre en contact avec l'aminosilane (A) ou avec tout agent durcisseur ou matériau contenant des groupes hydrolysables liés à un silicium faisant partie du polydiorganosiloxane (C) durcissable à la température ambiante.
- 10 15. Procédé selon la revendication 12, caractérisé en ce que l'on forme une composition de primaire pigmentée par dispersion d'un pigment dans un polydiorganosiloxane liquide à extrémités bloquées par des groupes hydroxyle et mélange de ce dernier avec l'aminosilane (A), la polyoléfine chlorée (B) et un agent durcisseur qui, avec le polydiorganosiloxane liquide à extrémités bloquées par des groupes hydroxyle, forme le polydiorganosiloxane (C) durcissable à la température ambiante, ladite étape de dispersion du pigment dans un polydiorganosiloxane liquide étant réalisée avant que le pigment n'entre en contact avec l'aminosilane (A) ou ledit agent durcisseur.
- 15 16. Procédé pour revêtir un substrat d'un caoutchouc silicone vulcanisable à la température ambiante, caractérisé en ce que le substrat est revêtu d'une composition de primaire selon l'une quelconque des revendications 1 à 11 et en ce que la composition de caoutchouc silicone vulcanisable à la température ambiante est appliquée par-dessus ladite composition de primaire.
- 20 17. Procédé selon la revendication 16, caractérisé en ce que la composition de primaire est telle que définie dans l'une quelconque des revendications 2 à 4 et la composition de caoutchouc silicone vulcanisable à la température ambiante comprend un alpha,oméga-dihydroxypolydiorganosiloxane utilisé en conjonction avec un agent durcisseur du même type que celui utilisé dans la composition de primaire.
- 25 18. Procédé selon la revendication 16, caractérisé en ce que la composition de primaire est telle que définie dans la revendication 5 ou la revendication 6 et la composition de caoutchouc silicone vulcanisable à la température ambiante comprend un polydiorganosiloxane à extrémités bloquées par des groupes hydrolysables liés à un silicium du même type que ceux présents dans le polydiorganosiloxane (C) durcissable à la température ambiante.
- 30
- 35
- 40
- 45
- 50
- 55