



Curable polysiloxane coating composition comprising polysilazane

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(54) Title: CURABLE POLYSILOXANE COATING COMPOSITION COMPRISING POLYSILAZANE

(57) Abstract: The present invention relates to a coating composition comprising a polysiloxane based binder system, wherein said binder system comprises a) one or more hydroxyl functional polysiloxane; and b) one or more organic polysilazane; wherein said one or more organic polysilazane constitutes 0.5-10 parts (weight) relative to 100 parts (weight) of said one or more hydroxyl functional polysiloxane. The coating composition is preferably a fouling release coating composition. The invention also relates to a structure, preferably a marine structure having on at least a part of the outer surface, a coat obtained from a coating composition according to the invention.

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CURABLE POLYSILOXANE COATING COMPOSITION COMPRISING POLYSILAZANE

FIELD OF THE INVENTION

The present invention relates to a coating composition comprising a polysiloxane based binder system, wherein said binder system comprises one or more hydroxyl functional polysiloxane; and one or more organic polysilazane. The invention further relates to a structure, preferably a marine structure, having on the outer surface a coat obtained from the coating composition of the invention. The coating composition is preferably a fouling release coating composition.

BACKGROUND OF THE INVENTION

Polysiloxane based coatings are widely used in fouling control coatings for marine structures. For example WO 2011/076856 discloses a fouling control coating composition comprising a polysiloxane-based binder system including hydrophilic-modified polysiloxanes and biocides; WO 2013/000479 discloses a cured coat comprising a polysiloxane-based binder matrix and one or more biocides, wherein the binder matrix has included as a part thereof hydrophilic oligomer/polymer moieties and WO 2013/000477 discloses a cured fouling control coat comprising a polysiloxane-based binder matrix and one or more enzymes for suppressing biofouling.

Typically such polysiloxane based coatings require a layer of tie-coat underneath to ensure adhesion to the underlying substrate. Experience has shown that while adhesion is generally satisfactory between the anticorrosive epoxy coating and the silicone based tie-coat, and between the silicone based tie-coat and the fouling release top-coat, adhesion between the fouling release top-coat and the anticorrosive epoxy coat is inferior.

Silicone based tie-coat compositions for use in fouling-release coating systems have been disclosed in for example WO 2010/018164 disclosing silicone based tie-coat compositions for fouling-release coating systems; and WO 2015/082408 disclosing a tie-coat suitable for overcoating an aged coating layer on a substrate. WO 2005/033219 discloses an epoxy-siloxane hybrid tie-coat and describes a typical coating system wherein a primer, a tie-coat and a topcoat is applied on a substrate.

Application of a tie-coat to obtain adhesion per se implies application of an extra coating layer which is both costly and time consuming, and requires more coating material as a full extra coating layer has to be applied. Furthermore, the tie-coats generally need to be specially designed for the substrate they are used on; which increases complexity and may compromise workability and efficiency.

There is a need for new silicone based coating compositions that combines the properties of a silicone based topcoat and a tie-coat, which would allow for application of fewer coating layers and provide a more simple coating system.

Moreover, for polysiloxane based coating compositions, curing speed and workability typically requires the use of tin-based, or other metal-based catalysts and high temperatures. These may be unwanted due to health and safety considerations for the people working with the systems. Thus, there is also a need for development of new curing processes for polysiloxane based coating compositions improving the safety conditions during handling and application.

10 SUMMARY OF THE INVENTION

The present invention provides a new silicone based coating composition with several advantages. E.g. the composition is cured at room temperature without the use of hazardous metal catalysts, and the composition provides a cured coat with good adhesion to various substrates, maintaining the qualities of a silicone based coat.

Accordingly, the present invention relates to a coating composition comprising a polysiloxane based binder system, wherein said binder system comprises

- a) one or more hydroxyl functional polysiloxane; and
- b) one or more organic polysilazane;

wherein said one or more organic polysilazane constitutes 0.5-10 parts (weight) relative to 100 parts (weight) of said one or more hydroxyl functional polysiloxane.

In one aspect, the invention relates to a kit of parts comprising

A) a first container comprising a composition comprising one or more hydroxyl functional polysiloxane; and B) a second container comprising a composition comprising one or more organic polysilazane;

or

a kit of parts comprising

A) a first container comprising a composition comprising one or more hydroxyl functional polysiloxane and one or more organic polysilazane; and B) a second container comprising one or more catalyst;

wherein said kit is for preparation of a coating composition according to the invention.

In one aspect, the invention relates to a marine structure having on at least a part of the outer surface, a cured coat obtained from a coating composition according to the invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a new polysiloxane based coating composition suitable for application on many different surfaces providing a coat with a good adhesion to a variety of substrates. The invention furthermore provides a curing process with advantages over the typically used curing process for polysiloxane based coating compositions

Accordingly, the invention relates to a coating composition comprising a polysiloxane based binder system, wherein said binder system comprises one or more hydroxyl functional polysiloxane; wherein said one or more organic polysilazane constitutes 0.5-10 parts (weight) relative to 100 parts (weight) of said one or more hydroxyl functional polysiloxane.

The inventors have developed a curing methodology for condensation of hydroxyl functional polysiloxane through the decomposition of organic polysilazanes. By adding small amounts of organic polysilazane to a mix of one or more hydroxyl functional polysiloxane components at ambient temperature, a spontaneous reaction forms a network that allows for curing of a soft film even at high dry film thickness (DFT). Although the reaction is spontaneous, the curing rate is increased by use of a catalyst. While many catalysts are useful to speed up the curing reaction, it has been found that primary/secondary amines, such as for example benzotriazole (BTZ) derivatives are particularly effective, even in small amounts. This reaction is particularly efficient towards carbinol functional polysiloxanes, for which it shows curing times suitable for coating use.

As a further advantage, small amounts of organic polysilazane used in the composition suffices to create a strong adhesion to the surface of many substrates not otherwise prone to be overcoated by silicone-based coatings. This means that the composition can be used on surfaces omitting a tie-coat. The substrate may be made of a single material such as for example metal, glass or plastic or it may be composed of various materials.

The claimed coating composition allows for curing of high film thicknesses and can therefore be used in situations where a thick film is needed such as for example for coating of marine structures. Obtaining a high film thickness with fewer application layers reduce the working time and omits the extra time needed for curing of individual layers before overcoating.

In addition to that, the coating composition is surprisingly also useful when a low thickness is required. This is of significant benefit for applications where for example transparency is of relevance, such as for non-stick coatings on clear substrates. Furthermore, since a tie coat is not necessary, and thus only a single coat is required, the transparency is even further improved.

Some coating systems combining silicone resins and polysilazane are known in the art. One example is JP2012153849 disclosing coating compositions comprising a polysilazane and a modified silicone oil and/or a curable silicone resin, for use in particular for vehicles, aircrafts, furniture, and outer walls of buildings. The polysilazane applied in the system is an inorganic polysilazane. These are

generally known for being very reactive and thus, difficult to handle (see e.g. Barosso et al., *Polysilazane-Based Coatings with Anti-Adherent Properties for Easy Release of Plastics and Composites from Metal Molds*, Adv. Mater. Interfaces (2020) 7, 1901952).

Organic polysilazanes applied in coatings have been disclosed for example in EP 3733801 and US 9676946. Both discloses coating compositions comprising the combination of polysilazane and silicone resins with polysilazane being the major component.

The coating composition of the current invention mainly constitute a polysiloxane-based binder system wherein organic polysilazane, used for promoting curing of the system, only constitutes a minor amount of the composition. The coating composition may be prepared from a range of different combinations of reactive polysiloxanes and polysilazanes.

Definition of substituents:

In the present context, "optionally substituted" means that the indicated moiety may or may not be substituted, typically on carbon atoms, and when substituted, a carbon atom may be mono-, di-, or tri-substituted when valency allows. It is understood that where no substituents are indicated for an "optionally substituted" moiety, then the position is held by a hydrogen atom.

The term "2-30-membered linear or branched saturated or unsaturated chain" refers to a linear (i.e. unbranched) or branched hydrocarbon having in the chain from 2 up to 30 atoms, inclusive; and optionally having one or more double bonds. The chain generally consists of hydrocarbons and may optionally contain one or more linkers selected independently from -O-, -S-, -N-, -N-C(O)-, -O-C(O)-, -N-C(O)-N- and -N-C(O)-O-. Chains solely consisting of hydrocarbon include linear or branched C₂-C₃₀ alkyl and linear or branched C₂-C₃₀ alkenyl. Examples of chains containing one or more linker include for example ethers and polyethers.

The term "3-30-membered saturated or unsaturated ring system" refers to a monocyclic ring system having from 3 up to 30 ring atoms, inclusive; and optionally having one or more double bonds. The ring generally consists of hydrocarbons and may optionally contain one or more linkers selected independently from -O-, -S-, -N-, -N-C(O)-, -O-C(O)-, -N-C(O)-N- and -N-C(O)-O-. Ring systems solely consisting of hydrocarbon include C₃-C₃₀ cycloalkyl; examples include (but are not limited to) monocyclic rings, fused ring systems, bridged ring systems and spirocyclic ring systems.

The term "aromatic ring system" in the present context refers to both monocyclic and fused C₆-C₃₀ membered aromatic rings. Examples include (but are not limited to) monocyclic aromatic rings such as for example benzene and bicyclic fused aromatic rings such as for example naphthalene.

The term "heteroaromatic ring system" in the present context refers to both monocyclic and fused C₅-C₃₀ membered aromatic rings containing at least one ring atom selected from O, N or S.

Examples include (but are not limited to) monocyclic heteroaromatic rings such as for example furan,

imidazole and pyridine and bicyclic fused aromatic rings such as for example indole, benzimidazole and quinoline.

The terms "halo" and "halogen" are used interchangeably and typically refer to fluorine, chlorine, bromine or iodine.

5 The terms "carbinol" and "silanol" are frequently used terms in connection with silicone chemistry. "carbinol" or "carbinol functional group" refers to a hydroxyl group bound to a carbon atom (C-OH) while "silanol" or "silanol functional group" refers to a hydroxyl group bound to a silicon atom (Si-OH).

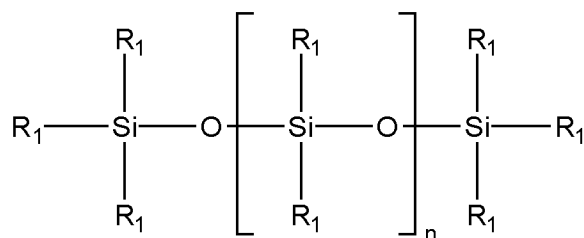
10 In the general formulas (Ia), (Ib) and (II) below it should be understood that all R groups are independently selected, also within the repeating units indicated by n, m and p. Thus for example in formula (Ia) R1 substituents may vary in between the repeating units (see also the illustrated polysiloxanes and polysilazanes used in the examples).

15 Polysiloxane:

The term 'polysiloxane' is known in the art and refers to polymers having a backbone in which atoms of silicon and oxygen alternate and which is devoid of carbon atoms (The New Encyclopedia Britannica in 30 volumes micropaedia volume IX. 1975 defining polysiloxane by referral to silicone). A polysiloxane backbone with organic (i.e. carbon-based) substituent on the silicon atom
20 may be referred to as a polyorganosiloxane. A commonly known polyorganosiloxane is polydimethylsiloxane (PDMS).

In the context of the invention, the binder system comprises a crosslinked polysiloxane binder system comprising one or more hydroxyl functional polysiloxane. The hydroxyl functional polysiloxane typically comprises one or more carbinol functional polysiloxane and/or one or more
25 silanol functional polysiloxane. In a preferred embodiment, said polysiloxane comprises at least one or more carbinol functional polysiloxane.

In one embodiment, the hydroxyl functional polysiloxane comprises a carbinol functional polysiloxane according to formula (Ia) below having a molecular weight in the range of 750 to 500,000 g/mol:



(Ia)

wherein n is an integer from 5 to 7500; and

wherein each R1 are independently selected from

methyl; or

a 2-30-membered linear or branched saturated or unsaturated chain consisting of carbon atoms and

5 optionally containing one or more linkers selected independently from -O-, -S-, -N-, -N-C(O)-, -O-C(O)-, -N-C(O)-N- and -N-C(O)-O-; or

a 3-30-membered saturated or unsaturated ring system consisting of carbon atoms and optionally containing one or more linkers selected independently from -O-, -S-, -N-, -N-C(O)-, -O-C(O)-, -N-C(O)-N- and -N-C(O)-O-; or

10 an aromatic or heteroaromatic ring system;

wherein each R1 may optionally be substituted one or more times with one or more substituents selected from halogen, hydroxyl, oxo and R2;

wherein each R2 are independently selected from

methyl; or

15 a 2-30-membered linear or branched saturated or unsaturated chain consisting of carbon atoms and optionally containing one or more linkers selected independently from -O-, -S-, -N-, -N-C(O)-, -O-C(O)-, -N-C(O)-N- and -N-C(O)-O-; or

a 3-30-membered saturated or unsaturated ring system consisting of carbon atoms and optionally containing one or more linkers selected independently from -O-, -S-, -N-, -N-C(O)-, -O-C(O)-, -N-C(O)-N- and -N-C(O)-O-; or

20 an aromatic or heteroaromatic ring system;

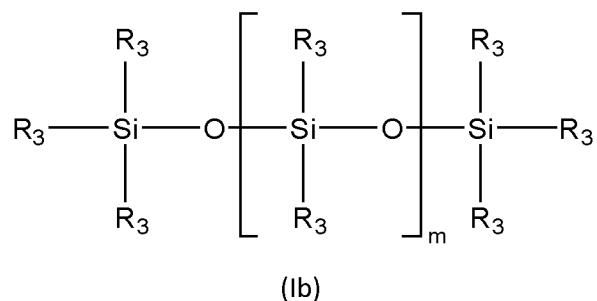
wherein said R2 may optionally be substituted one or more times with halogen, hydroxyl and oxo; and

wherein each optionally substituted R1 is having a Mw of <500 g/mol;

25 with the proviso that at least one R1 and/or R2 has at least one carbinol functional group.

Commercially available carbinol functional polysiloxanes suitable for the present invention include DMS C21 and C23 from Gelest; and Silmer OHT Di-400, Silmer OH C50, Silmer OH J10, and Silmer OHT E13 from Siltech.

30 In one embodiment, the hydroxyl functional polysiloxane comprises a silanol functional polysiloxane according to formula (Ib) below having a molecular weight in the range of 750 to 500,000 g/mol:



wherein m is an integer from 5 to 7500;

wherein each R₃ are independently selected from hydroxyl, methyl or linear or branched C₁-C₃₀ alkyl,

5 linear or branched C₂-C₃₀ alkenyl, C₃-C₃₀ cycloalkyl or aryl;

with the proviso that at least two R₃ groups are hydroxyl groups.

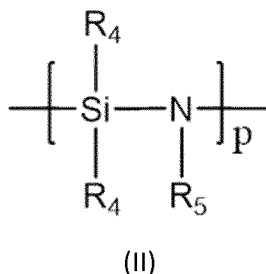
Commercially available hydroxyl functional polysiloxanes suitable for the present invention include polydimethylsiloxanes (PDMS) from Gelest, such as DMS S14, S15, S21 and S31 from Gelest and Siltech S-701, S-5000 and S-20000 from Siltech

10

Polysilazane:

Polysilazanes are silicon-based polymers containing alternating silicon and nitrogen atoms in their backbone. Polysilazane compounds in the present context include compounds having a chain structure, a cyclic structure, or a structure in which molecules are crosslinked to each other.

15 The polysilazane compound used in the present invention is typically a compound according to formula (II) below:



wherein p is an integer from 5 to 100;

20 wherein each R₄ are independently selected from hydrogen, linear or branched C₁-C₆ alkyl or linear or branched C₁-C₆ alkenyl; and

each R₅ are independently selected from hydrogen, linear or branched C₁-C₆ alkyl or linear or branched C₁-C₆ alkenyl.

A compound in which all of R₄ and R₅ represent hydrogen atoms is generally referred to as an inorganic polysilazane or a perhydropolysilazane, while compounds containing at least one organic group as any one of R₄ and R₅ are generally referred to as organic polysilazanes or organopolysilazanes. In the present invention, the polysilazane is preferably an organic polysilazane.

25

In a preferred embodiment, at least one of R4 are selected from methyl, ethyl, and vinyl. In an even more preferred embodiment, at least one of R4 is a vinyl. In a preferred embodiment, R5 is hydrogen.

The polysilazane may be appropriately selected according to characteristics required for a cured product. Mixtures of one or more polysilazane may be used.

Commercially available polysilazanes suitable for the present invention include organic polysilazanes: Durazane 1033, Durazane 1066, Durazane 1800 from Merck, IOTA-OPSZ-9150 and IOTA-OPSZ-9108 from IOTA Silicone Oil (Anhui) Co. Ltd., and Octamethylcyclotetrasilazane from Merck, Germany.

The polysiloxane-based binder system typically constitutes at least 40 % by dry weight, such as 40-98 % by dry weight, or 45-95 % by dry weight, or 50-95 % by dry weight, in particular 50-90 % by dry weight, or 55-90 % by dry weight, or 60-90 % by dry weight, of the coating composition.

Catalyst

In one embodiment, a catalyst is applied to accelerate the reaction between the one or more polysiloxane and the one or more polysilazane.

The catalyst is typically selected from conventionally known compounds used as catalysts in condensation reactions. For example, from inorganic acid compounds, organic acid compounds, inorganic base compounds and organic base compounds. Examples of inorganic acid compounds include, but are not limited to, hydrochloric acid, phosphoric acid, sulfuric acid, hydrofluoric acid. Examples of organic acid compounds include p-toluenesulfonic acid, oxalic acid, acetic acid. Examples of inorganic base compounds include, but are not limited to, ammonia and sodium hydroxide. Examples of organic base compounds include, but are not limited to, trimethylamine, triethylamine, tributylamine, 1,5-diazabicyclo [4.3.0] nonene-5 (DBN), 1,8-diazabicyclo [5.4.0] undecene-7 (DBU), 1,1,3,3-tetramethylguanidine, di-methyl amino pyridine (DMAP), andazole derivatives such as imidazole and imidazole derivatives and benzotriazole and benzotriazole derivatives.

Organic metal catalysts may also be used, such as for example organic tin compounds, organic zinc compounds, organic titanium compounds, organic zirconium compounds, organic aluminum compounds, and organic nickel compounds. Examples of organic tin compounds include, but are not limited to, dibutyltin dilaurate, dibutyltin dioctate, dibutyltin diacetate, dioctyltin dilaurate, dioctyltin dioctate, dioctyltin diacetate, dibutyltin bisacetylacetate. Examples of organic zinc compounds include, but are not limited to, zinc acetylacetonate, zinc-2-ethylhexoate, zinc naphthenate, zinc stearate. Examples of organic bismuth compounds include, but are not limited to, bismuth 2-ethylhexanoate, bismuth octanoate, bismuth neodecanoate. Examples of organic titanium

compounds include, but are not limited to, tetrabutyl titanate, tetranonyl titanate, tetrakis ethylene glycol methyl ether titanate, Titanium diisopropoxide bis(acetylacetonate). Examples of organic zirconium compounds include, but are not limited to, zirconium tetraacetylacetonate, zirconium tributoxy acetylacetonate, zirconium dibutoxy diacetylacetonate, zirconium tetra propoxide, zirconium tetra butoxide, zirconium octoate. Examples of organic aluminum compounds include, but are not limited to, aluminum salts such as aluminum octylate, aluminum triacetate, or aluminum tristearate; aluminum alkoxides such as aluminum trimethoxide, aluminum triethoxide, aluminum ethoxybis(acetylacetonate), aluminum butoxybis(ethylacetoacetate), aluminum dimethoxy (ethylacetoacetate), aluminum diisopropoxy (ethylacetoacetate), aluminum tris(ethylacetoacetate), aluminum tris(acetylacetonate). Examples of organic nickel compounds include, but are not limited to, nickel (II) acetylacetonate, nickel (II) hexafluoroacetylacetonate hydrate.

According to the present invention, the catalyst is preferably an organic base compound, and particularly preferably an amine compound. Preferably said catalyst is a basic catalyst, more preferably an azole derivative such as benzotriazole or a benzotriazole derivative; or a cyclic amine such as DBU; or di-methyl amino pyridine (DMAP).

It is a pre-requisite that the catalyst, if present, is compatible with the coating system. It is within the capability of the skilled person to select an appropriate catalyst. In one embodiment a catalyst is not included, i.e. the curing reaction takes place without the use of a catalyst.

The catalyst may be used alone or as combination of two or more catalysts. The amount of catalyst to be used is depending on the reactivity of the catalyst and the cross-linker(s) and desired curing time. In a preferred embodiment the catalyst concentration is between 0.0001-5.0 %, e.g. 0.0001-2.0 %, or 0.005-5 %, or 0.01-4.0 %, or 0.1-3.0 %, by dry weight of the coating composition; or in an amount of 0.0001-0.001%, or 0.0001-0.01% or 0.0001-1.0% by dry weight of the coating composition.

A catalyst is preferably included when the hydroxyl functional polysiloxane mainly comprises silanol functional polysiloxane.

Further components

The coating composition typically comprises further components selected from fillers, pigments, additives and solvents.

Pigments and fillers are in the present context viewed in conjunction as constituents that may be added to the coating composition with only limited implications on the adhesion properties. "Pigments" are normally characterised in that they render the final coating non-transparent and non-

translucent, whereas "fillers" normally are characterised in that they do not render the coating non-translucent and therefore do not contribute significantly to hide any material below the coating.

Examples of pigments are grades of titanium dioxide, red iron oxide, zinc oxide, carbon black, graphite, yellow iron oxide, red molybdate, yellow molybdate, zinc sulfide, antimony oxide, sodium aluminium sulfosilicates, quinacridones, phthalocyanine blue, phthalocyanine green, black iron oxide, indanthrone blue, cobalt aluminium oxide, carbazole dioxazine, chromium oxide, isoindoline orange, bis-acetoacet-o-tolidiole, benzimidazolone, quinaphthalone yellow, isoindoline yellow, tetrachloro-isoindolinone, quinophthalone yellow.

Examples of fillers are calcium carbonate such as calcite, dolomite, talc, mica, feldspar, barium sulfate, kaolin, nephelin, silica (including hydrophilic and hydrophobic silica), perlite, magnesium oxide, and quartz flour, etc. Fillers (and pigments) may also be added in the form of nanotubes or fibers, thus, apart from the before-mentioned examples of fillers, the coating composition may also comprise fibers, e.g. those generally and specifically described in WO 00/77102 which is hereby incorporated by reference.

Any pigments and/or fillers typically constitute 0-60 %, such as 0-50 %, preferably 5-45 %, such as 5-40 %, or 5-35 %, or 0.5-25 %, or 1-20 %, by dry weight of the coating composition. Taking into account the density of any pigments and/or fillers, such constituents typically constitute 0.2-20 %, such as 0.5-15 % by solids volume of the coating composition.

Examples of additives are:

- (i) non-reactive fluids such as non-reactive organopolysiloxanes; for example polydimethylsiloxane, methylphenyl polysiloxane; petroleum oils and combinations thereof;
- (ii) surfactants such as derivatives of propylene oxide or ethylene oxide such as alkylphenol-ethylene oxide condensates (alkylphenol ethoxylates); ethoxylated monoethanolamides of unsaturated fatty acids such as ethoxylated monoethanolamides of linoleic acid; sodium dodecyl sulfate; and soya lecithin;
- (iii) wetting agents and dispersants such as those described in M. Ash and I. Ash, "Handbook of Paint and Coating Raw Materials, Vol. 1", 1996, Gower Publ. Ltd., Great Britain, pp 821-823 and 849-851;
- (iv) thickeners and anti-settling agents (e.g. thixotropic agents) such as colloidal silica, hydrated aluminium silicate (bentonite), aluminium tristearate, aluminium monostearate, xanthan gum, chrysotile, pyrogenic silica, hydrogenated castor oil, organo-modified clays, polyamide waxes and polyethylene waxes;
- (v) dyes such as 1,4-bis(butylamino)anthraquinone and other anthraquinone derivatives; toluidine dyes, etc.; and
- (vi) antioxidants such as bis(tert-butyl) hydroquinone, 2,6-bis(tert-butyl) phenol, resorcinol, 4-tert-butyl catechol, tris(2,4-di-tert-butylphenyl)phosphite, pentaerythritol Tetrakis(3-(3,5-di-tert-butyl-4-

hydroxyphenyl)propionate), bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, etc.

(vii) Release oils such as those described in US6107381, WO2011076856 or GB1470465, capable of blooming to the surface of the coating, thereby altering the surface properties. The oils are selected so that they do not contain groups that can react with the binder system or any individual binder components. Hence the oils are intended to be non-reactive, such that the oils do not become covalently linked to the binder system, but instead are freely embedded into the binder film in which such oils in principles may migrate more or less freely.

Any additives typically constitute 0-30 %, such as 0-15 %, by dry weight of the coating composition. Preferably, the coating composition comprises one or more thickeners and/or anti-settling agents (e.g. thixotropic agents), preferably in an amount of 0.2-10 %, such as 0.5-5 %, e.g. 0.6-4 %, by dry weight of the coating composition.

Moreover, the coating composition may be supplemented with one or more solvents. Examples of solvents are aliphatic, cycloaliphatic and aromatic hydrocarbons such as white spirit, cyclohexane, toluene, xylene and naphtha solvent, esters such as methoxypropyl acetate, n-butyl acetate and 2-ethoxyethyl acetate; and mixtures thereof. Alternatively, the solvent system may include water or be water-based (>50% water in the solvent system). Preferably the solvents have a boiling point of 110 °C or more. The solvents, if any, typically constitute 5-50 % by volume of the coating composition.

With the aim of facilitating easy application of the coating composition (e.g. by spray, brush or roller application techniques), the coating composition typically has a viscosity in the range of 25-25,000 mPa·s, such as in the range of 150-15,000 mPa·s, in particular in the range of 200-4,000 mPa·s.

Fouling release coat

In one embodiment, the claimed coating composition is intended for use as a fouling release coating composition, thus providing a cured coat with fouling release properties, i.e. a fouling release coat.

In the context of the invention, "fouling-release" (as well as "fouling control") relates to all types of bio-fouling (i.e. settlement of organisms on a surface) of a surface exposed to an aqueous environment or to aqueous liquids (e.g. within tanks, pipes, etc.). It is however, believed that the coatings defined herein are particularly relevant for avoiding or reducing marine bio-fouling, i.e. bio-fouling arising in connection with the exposure of a surface to a marine environment, in particular to sea-water. In a preferred embodiment, said fouling release coat is applied directly onto the substrate without an intermediate tie coat.

Biocides

In one embodiment, the fouling release coat may further comprise one or more biocides. In the present context, the term "biocide" is intended to mean an active substance intended to destroy, deter, render harmless, prevent the action of, or otherwise exert a controlling effect on any harmful organism by chemical or biological means. It should be understood, that the biocide(s) is not a mandatory constituent according to the invention as the claimed coating in itself possess fouling release properties.

Illustrative examples of biocides are those selected from metallo-dithiocarbamates such as bis(dimethyldithiocarbamato)zinc, ethylene-bis(dithiocarbamato)zinc, ethylene-bis(dithiocarbamato)manganese, and complexes between these; bis(1-hydroxy-2(1H)-pyridine-thionato-0,S)-copper; copper acrylate; bis(1-hydroxy-2(1H)-pyridinethionato-0,S)-zinc; phenyl(bispyridyl)-bismuth dichloride; metal biocides such as copper(I)oxide, cuprous oxide, metallic copper, copper metal alloys such as copper-nickel alloys; metal salts such as cuprous thiocyanate, basic copper carbonate, copper hydroxide, barium metaborate, and copper sulphide; heterocyclic nitrogen compounds such as 3a,4,7,7a-tetrahydro-2-((trichloro-methyl)-thio)-1H-isoindole-1,3(2H)-dione, pyridine-triphenylborane, 1-(2,4,6-trichloro-phenyl)-1H-pyrrole-2,5-dione, 2,3,5,6-tetrachloro-4-(methylsulfonyl)-pyridine, 2-methylthio-4-tert-butylamino-6-cyclopropylamine-s-triazin, and quinoline derivatives; heterocyclic sulfur compounds such as 2-(4-thiazolyl)benzimidazole, 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one, 4,5-dichloro-2-octyl-3(2H)-isothiazoline (Sea-Nine[®]-211N), 1,2-benzisothiazolin-3-one, and 2-(thiocyanatomethylthio)-benzothiazole; urea derivatives such as N-(1,3-bis(hydroxyl-methyl)-2,5-dioxo-4-imidazolidinyl)-N,N'-bis(hydroxymethyl)urea, and N-(3,4-dichloro-phenyl)-N,N-dimethylurea, N,N-dimethylchlorophenylurea; amides or imides of carboxylic acids; sulfonic acids and of sulfenic acids such as 2,4,6-trichlorophenyl maleimide, 1,1-dichloro-N-((dimethylamino)sulfonyl)-1-fluoro-N-(4-methylphenyl)-methanesulfenamide, 2,2-dibromo-3-nitrilopropionamide, N-(fluorodichloromethylthio)-phthalimide, N,N-dimethyl-N'-phenyl-N'-(fluorodichloromethylthio)-sulfamide, and N-methylol formamide; salts or esters of carboxylic acids such as 2-((3-iodo-2-propynyl)oxy)-ethanol phenylcarbamate and N,N-didecyl-N-methylpoly(oxyethyl)ammonium propionate; amines such as dehydroabiethyl-amines and cocodimethylamine; substituted methane such as di(2-hydroxy-ethoxy)methane, 5,5'-dichloro-2,2'-dihydroxydiphenylmethane, and methylene-bisthiocyanate; substituted benzene such as 2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile, 1,1-dichloro-N-((dimethyl-amino)-sulfonyl)-1-fluoro-N-phenylmethanesulfenamide, and 1-((diiodomethyl)sulfonyl)-4-methyl-benzene; tetraalkyl phosphonium halogenides such as tri-n-butyltetradecyl phosphonium chloride; guanidine derivatives such as n-dodecylguanidine hydrochloride; disulfides such as bis-(dimethylthiocarbamoyl)-disulfide, tetramethylthiuram disulfide; imidazole containing compounds, such as medetomidine; 2-(p-chlorophenyl)-3-cyano-4-bromo-5-trifluoromethyl pyrrole and mixtures thereof.

It is preferred that the biocide (if at all present) does not comprise tin. Currently preferred biocides are those selected from the group consisting of 2,4,5,6-tetra-chloroisophthalonitrile (Chlorothalonil), copper thiocyanate (cuprous sulfocyanate), N-dichloro-fluoromethylthio-N',N'-dimethyl-N-phenylsulfamide (Dichlofluanid), 3-(3,4-dichlorophenyl)-1,1-dimethylurea (Diuron), N²-tert-butyl-N⁴-cyclopropyl-6-methylthio-1,3,5-triazine-2,4-diamine (Cybutryne), 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile, (2-(p-chlorophenyl)-3-cyano-4-bromo-5-trifluoromethyl pyrrole; Tralopyril), N²-tert-butyl-N⁴-cyclopropyl-6-methylthio-1,3,5-triazine-2,4-diamine (Cybutryne), (RS)-4-[1-(2,3-dimethylphenyl)ethyl]-3H-imidazole (Medetomidine), 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT, Sea-Nine[®] 211N), dichlor-N-((dimethylamino)sulfonyl)fluor-N-(p-tolyl)methansulfenamid (Tolylfluanid), 2-(thiocyanomethylthio)-1,3-benzothiazole ((2-benzothiazolylthio)methyl thiocyanate; TCMTB), triphenylborane pyridine (TPBP); bis(1-hydroxy-2(1H)-pyridinethionato-0,S)-(T-4) zinc (zinc pyridinethione; zinc pyrithione), bis(1-hydroxy-2(1H)-pyridinethionato-0,S)-T-4 copper (copper pyridinethione; copper pyrithione), zinc ethylene-1,2-bis-dithiocarbamate (zinc-ethylene-N-N'-dithiocarbamate; Zineb), copper(II) oxide, metallic copper, 3-(3,4-dichlorophenyl)-1,1-dimethylurea (Diuron) and diiodomethyl-p-tolylsulfone; Amical 48.

The biocides are preferably selected among biocides which are effective against soft fouling such as slime and algae. Examples of such biocides are N²-tert-butyl-N⁴-cyclopropyl-6-methylthio-1,3,5-triazine-2,4-diamine (Cybutryne), 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT, Sea-Nine[®] 211N), bis(1-hydroxy-2(1H)-pyridinethionato-0,S)-(T-4) zinc (zinc pyridinethione; zinc pyrithione), bis(1-hydroxy-2(1H)-pyridinethionato-0,S)-T-4 copper (copper pyridinethione; copper pyrithione; Copper Omadine) and zinc ethylene-1,2-bis-dithiocarbamate (zinc-ethylene-N-N'-dithiocarbamate; Zineb), copper(I) oxide, metallic copper, copper thiocyanate, (cuprous sulfocyanate), bis(1-hydroxy-2(1H)-pyridinethionato-0,S)-T-4 copper (copper pyridinethione; copper pyrithione; Copper Omadine).

Most preferably, the biocide is an organic biocide, such as a pyrithione complex, such as zinc pyrithione, or such as copper pyrithione. Organic biocides are those either fully or in part being of organic origin. As detailed in US 7,377,968, in those instances in which the biocide is depleted rapidly from the film due to e.g. a high water solubility or a high level of immiscibility with the matrix composition, it can be advantageous to add one or more of the biocide(s) in encapsulated form as a means of controlling the biocide dosage and extending the effective lifetime in the film. Encapsulated biocides can also be added if the free biocide alters the properties of the polysiloxane matrix in a way that is detrimental for its use as antifouling coatings (e.g. mechanical integrity, drying times, etc.).

The biocide preferably has a solubility in the range of 0-20 mg/L, such as 0.00001-20 mg/L, in water at 25 °C. If present, the biocide typically constitutes 0.1-15 % by dry weight, e.g. 0.5-8 % by dry weight, in particular 1-6 % by dry weight, of the coating composition.

5 Preparation of the coating composition

The coating composition may be prepared by any suitable technique that is commonly used within the field of paint production. Thus, the various constituents may be mixed together utilizing a mixer, a high speed disperser, a ball mill, a pearl mill, a grinder, a three-roll mill etc. The coating compositions may be prepared and shipped as two- or three-component systems that should be combined and thoroughly mixed immediately prior to use. Thus, the invention also relates to a kit of parts comprising two or three containers comprising components for the coating composition. In one embodiment, the invention relates to a kit of parts comprising a first container containing the one or more hydroxyl functional polysiloxane; and another container comprising the one or more polysilazane. The first container may further comprise one or more catalyst, alternative the kit may comprise a third container comprising one or more catalyst. In another embodiment, the kit comprises a first container comprising one or more hydroxyl functional polysiloxane, preferably a silanol functional polysiloxane, and the one or more polysilazane; and a second container comprising one or more catalyst. In a separate embodiment, the coating composition is a one-component composition. Whether shipment must be performed in separate containers depends on the exact combination of polysiloxane and polysilazane. The coating compositions according to the invention may be filtrated using bag filters, patron filters, wire gap filters, wedge wire filters, metal edge filters, EGLM turnoclean filters (ex. Cuno), DELTA strain filters (ex. Cuno), and Jenag Strainer filters (ex. Jenag), or by vibration filtration. An example of a suitable preparation method is described in the Examples.

25 The coating composition is typically prepared by mixing two or more components e.g. two pre-mixtures, one pre-mixture comprising the one or more reactive polysiloxane and the optional catalyst, and one pre-mixture comprising the one or more polysilazane. Both pre-mixtures may optionally comprise components selected from solvents, additives, fillers and pigments.

It should be understood that when reference is made to the "coating composition", it refers to the mixed composition comprising all constituents including the polysiloxane and the polysilazanes and optional catalyst and solvent, additives, fillers, pigments, ready to be applied on a substrate. Furthermore, all amounts stated as % by dry weight of the coating composition should be understood as % by dry weight of the mixed coating composition ready to be applied, i.e. the weight apart from the solvents (if any).

Application of the coating composition

The coating composition of the invention is typically applied to at least a part of the surface of a substrate.

5 The term “applying” is used in its normal meaning within the paint industry. Thus, “applying” is conducted by means of any conventional means, e.g. by brush, by roller, by spraying, by dipping, etc. The commercially most interesting way of “applying” the coating composition is by spraying. Hence, the coating composition is preferably sprayable. Spraying is effected by means of conventional spraying equipment known to the person skilled in the art. The coating is typically
10 applied in a dry film thickness of 10-600 μm , such as 50-500 μm , such as 50-400 μm , e.g. 75-300 μm , or 20-200, such as 20-100 μm .

 Moreover, the coating composition is preferably such with respect to sag resistance cf. ASTM D 4400-99 (i.e. relating to its ability to be applied in a suitable film thickness to a vertical surface without sagging) that it exhibits sag resistance for a wet film thickness up to at least 70 μm , such as
15 up to at least 200 μm , preferably up to at least 400 μm , and in particular up to at least 500 μm .

 The term “at least a part of the surface of a substrate” refers to the fact that the coating composition may be applied to any fraction of the surface. For many applications, the coating composition is at least applied to the part of the substrate (e.g. a vessel) where the surface (e.g. the ship’s hull) may come in contact with water, e.g. sea-water.

20 The term “substrate” is intended to mean a solid material onto which the coating composition is applied. The substrate typically comprises a metal such as steel, iron, aluminum, bronze or glass-fiber reinforced polyester. Alternatively other substrates may also be relevant such as plastic substrates comprising for example poly (ethylene terephthalate) (PET), polypropylene (PP), acryl or other plastic materials. In the most interesting embodiments, the substrate is a metal
25 substrate, in particular a steel or a bronze substrate. In an alternative embodiment, the substrate is a glass-fiber reinforced polyester substrate. In some embodiments, the substrate is at least a part of the outermost surface of a marine structure.

 The term “surface” is used in its normal sense, and refers to the exterior boundary of an object. Particular examples of such surfaces are the surface of marine structures, such as vessels
30 (including but not limited to boats, yachts, motorboats, motor launches, ocean liners, tugboats, tankers, container ships and other cargo ships, submarines, and naval vessels of all types), pipes, shore and off-shore machinery, constructions and objects of all types such as piers, pilings, bridge substructures, water-power installations and structures, underwater oil well structures, nets and buoys, etc.

The surface of the substrate may preferably be the “native” surface (e.g. a steel surface or a glass-fiber reinforced polyester surface). An advantage of the claimed polysiloxane based coating composition is the good adhesion to various substrates without the need of a tie coat. However, the substrate may in some instances have a coating layer for example an anticorrosive coating and/or a tie coat, so that the surface of the substrate is constituted by such a coating. When present, the (anticorrosive and/or tie) coating is typically applied in a total dry film thickness of 100-600 µm, such as 150-450 µm, e.g. 200-400 µm. Alternatively, the substrate may have an older coating applied on the surface, e.g. a worn-out fouling control coat, or similar.

In one important embodiment, the substrate is a metal substrate (e.g. a steel or a bronze substrate) coated with an anticorrosive coating such as an anticorrosive epoxy-based coating, e.g. cured epoxy-based coating, or a shop-primer, e.g. a zinc-rich shop-primer. In another relevant embodiment, the substrate is a glass-fiber reinforced polyester substrate coated with an epoxy primer coating.

Embodiments of the invention

In the following, embodiments of the invention are disclosed. It should be understood that the various aspects, embodiments, implementations and features of the invention mentioned herein may be claimed separately, or in any combination.

In one aspect, the invention relates to a coating composition comprising a polysiloxane based binder system, wherein said binder system comprises

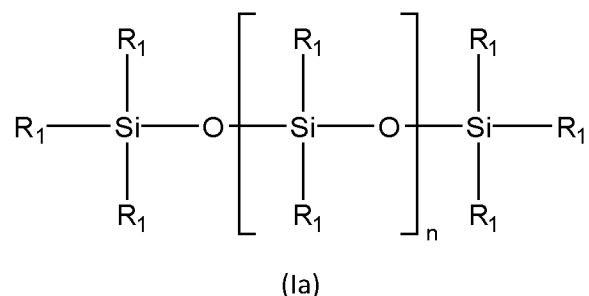
- a) one or more hydroxyl functional polysiloxane; and
- b) one or more organic polysilazane;

wherein said one or more organic polysilazane constitutes 0.5-10 parts (weight) relative to 100 parts (weight) of said one or more hydroxyl functional polysiloxane.

In one embodiment, said one or more hydroxyl functional polysiloxane comprises a1) one or more carbinol functional polysiloxane, and/or a2) one or more silanol functional polysiloxane. In a further embodiment said one or more hydroxyl functional polysiloxane comprises a1) one or more carbinol functional polysiloxane, and optionally a2) one or more silanol functional polysiloxane.

In one embodiment, said one or more organic polysilazane constitutes 1-10 parts (weight), such as 2-10 parts (weight), such as 3-10 parts (weight), such as 4-10 parts (weight), such as 0.5-9 parts (weight), such as 0.5-8 parts (weight), or 0.5-7 parts (weight), or 1-9 parts (weight), or 1-8 parts (weight), or 1-7 parts (weight) or 2-9 parts (weight), preferably 2-8 parts (weight), or 2-7 parts (weight) relative to 100 parts (weight) of said one or more hydroxyl functional polysiloxane.

In one embodiment, said hydroxyl functional polysiloxane comprises a carbinol functional polysiloxane. In a preferred embodiment, said carbinol functional polysiloxane is represented by formula (Ia) below having a molecular weight in the range of 750 to 500,000 g/mol:



5

wherein n is an integer from 5 to 7500; and

wherein each R1 are independently selected from methyl; or

10 a 2-30-membered linear or branched saturated or unsaturated chain consisting of carbon atoms and optionally containing one or more linkers selected independently from -O-, -S-, -N-, -N-C(O)-, -O-C(O)-, -N-C(O)-N- and -N-C(O)-O-; or

a 3-30-membered saturated or unsaturated ring system consisting of carbon atoms and optionally containing one or more linkers selected independently from -O-, -S-, -N-, -N-C(O)-, -O-C(O)-, -N-C(O)-N- and -N-C(O)-O-; or

15 an aromatic or heteroaromatic ring system;

wherein each R1 may optionally be substituted one or more times with one or more substituents selected from halogen, hydroxyl, oxo and R2;

wherein each R2 are independently selected from methyl; or

20 a 2-30-membered linear or branched saturated or unsaturated chain consisting of carbon atoms and optionally containing one or more linkers selected independently from -O-, -S-, -N-, -N-C(O)-, -O-C(O)-, -N-C(O)-N- and -N-C(O)-O-; or

a 3-30-membered saturated or unsaturated ring system consisting of carbon atoms and optionally containing one or more linkers selected independently from -O-, -S-, -N-, -N-C(O)-, -O-C(O)-, -N-C(O)-N- and -N-C(O)-O-; or

25

an aromatic or heteroaromatic ring system;

wherein said R2 may optionally be substituted one or more times with halogen, hydroxyl and oxo; and

wherein each optionally substituted R1 is having a Mw of <500 g/mol;

30 with the proviso that at least one R1 and/or R2 has at least one carbinol functional group.

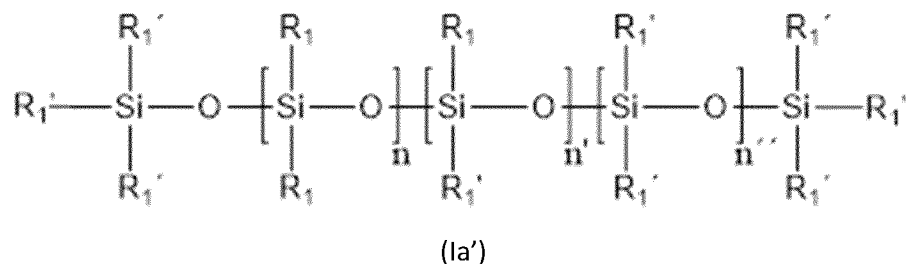
In one embodiment the molecular weight of the compound of formula (Ia) is in the range of 1000 to 500,000 g/mol, such as 1000 to 100,000 g/mol, 5000 to 100,000 g/mol or 5000 to 50,000 g/mol. In one embodiment, each optionally substituted R1 is having a Mw of <450 g/mol, such as <400 g/mol, such as <350 g/mol, such as <300 g/mol. In one embodiment, n is an integer from 5 to 5000; such as from 5 to 4000, such as from 5-3000, such as from 5-2000, preferably from 5 to 1000, more preferably from 20 to 1000 or from 20 to 500. In a preferred embodiment, the molecular weight of the compound of formula (Ia) is in the range of 1000 to 500,000 g/mol, such as 1000 to 100,000 g/mol, 5000 to 100,000 g/mol or 5000 to 50,000 g/mol, and each optionally substituted R1 is having a Mw of <450 g/mol, such as <400 g/mol, such as <350 g/mol, such as <300 g/mol; and n is an integer from 5 to 5000; such as from 5 to 4000, such as from 5-3000, such as from 5-2000, preferably from 5 to 1000, more preferably from 20 to 1000 or from 20 to 500.

In one embodiment, each R1 are independently selected from methyl; or a 2-30-membered linear or branched saturated or unsaturated chain consisting of carbon atoms and optionally containing one or more linkers selected independently from -O-, -S-, -N-C(O)-, -C-O-C(O)- and -N-C(O)-O-; or a 3-30-membered saturated or unsaturated ring system consisting of carbon atoms and optionally containing one or more linkers selected independently from -O-, -S-, -N-C(O)-, -C-O-C(O)- and -N-C(O)-O-; wherein said methyl and said 2-30-membered linear or branched saturated or unsaturated chain and said 3-30-membered saturated or unsaturated ring may optionally be substituted one or more times with one or more R2; wherein each R2 is independently selected from halogen, hydroxyl and oxo; with the proviso that at least one R1 and/or R2 has at least one carbinol functional group.

In a preferred embodiment, each R1 is independently selected from unsubstituted methyl or an unsubstituted 2-10 membered linear or branched saturated or unsaturated chain consisting of carbon atoms and optionally containing one or more linkers selected independently from -O-, -S-, -N-C(O)-, -C-O-C(O)- and -N-C(O)-O-. When one or more linkers are present, said linker is preferably -O-.

In one embodiment, at least two of R1 and/or R2 are having at least one carbinol functional group, or at least three of R1 and/or R2 are having at least one carbinol functional group, or at least one of R1 and/or R2 is having at least two carbinol functional groups, or at least one of R1 and/or R2 are having at least three carbinol functional groups, or at least two of R1 and/or R2 are having at least two carbinol functional groups. In a further embodiment, the remaining R1 are all selected independently from unsubstituted C₁-C₆ alkyl, preferably unsubstituted methyl.

In a further embodiment, said carbinol functional polysiloxane is represented by formula (Ia') below having a molecular weight in the range of 750 to 500,000 g/mol:



wherein $(n+n'+n'')$ is an integer from 5 to 7500; and

wherein $(n'+n'')$ is an integer from 0-50,

5 R1 and R2 are as defined for compound (Ia); and

any R2 substituent on R1' is denoted R2', and R1' and R2' are as defined R1 and R2 in compound (Ia), with the proviso that at least one of R1' and/or R2' is having at least one carbinol functional group and none of R1 and R2 can have a carbinol functional group.

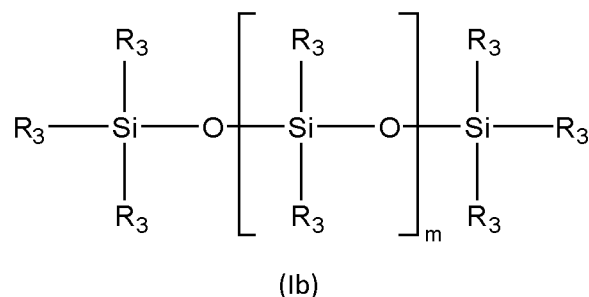
10 In one embodiment, the molecular weight of the compound of formula (Ia') is in the range of 1000 to 500,000 g/mol, such as 1000 to 100,000 g/mol, 5000 to 100,000 g/mol or 5000 to 50,000 g/mol.

15 In one embodiment, $(n+n'+n'')$ is an integer from 5 to 5000; such as from 5 to 4000, such as from 5-3000, such as from 5-2000, preferably from 5 to 1000, more preferably from 20 to 1000 or from 20 to 500; and $(n'+n'')$ is an integer from 0-40, such as from 0-30, such as from 0-20, preferably from 0-10.

20 In the compound of formula (Ia') in one embodiment, at least two of R1' and/or R2' are having at least one carbinol functional group, or at least three of R1' and/or R2' are having at least one carbinol functional group, or at least one of R1' and/or R2' is having at least two carbinol functional groups, or at least one of R1' and/or R2' are having at least three carbinol functional groups, or at least two of R1' and/or R2' are having with at least two carbinol functional groups. In a further embodiment, the remaining of R' and/or R2' are all selected from unsubstituted C₁-C₆ alkyl, preferably unsubstituted methyl. In a further embodiment, R1 are all selected independently from unsubstituted C₁-C₆ alkyl, preferably all R1 are unsubstituted methyl.

25 In a preferred embodiment, the number of carbinol groups in the carbinol functional polysiloxane is between 1-100, such as between 1-50, such as between 1-25 or 1-10.

In one embodiment, said hydroxyl functional polysiloxane comprises a silanol functional polysiloxane. In a preferred embodiment, said silanol functional polysiloxane is represented by formula (Ib) below having a molecular weight in the range of 750 to 500,000 g/mol:



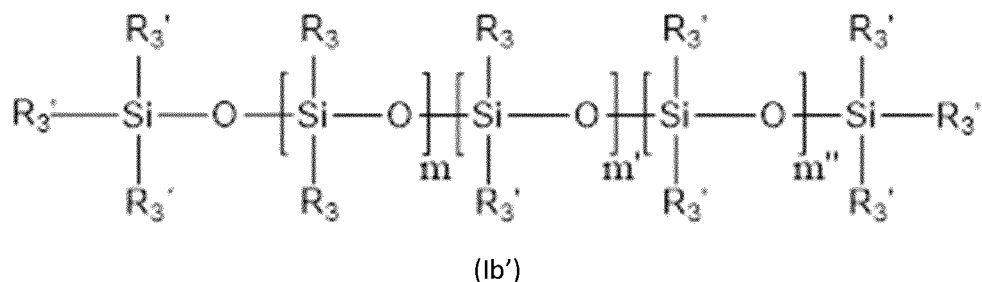
wherein m is an integer from 5 to 7500;

- 5 wherein each R₃ are independently selected from hydroxyl, methyl or linear or branched C₁-C₃₀ alkyl, linear or branched C₂-C₃₀ alkenyl, C₃-C₃₀ cycloalkyl or aryl; with the proviso that at least two R₃ groups are hydroxyl groups.

In one embodiment, the molecular weight of the compound of formula (Ib) is in the range of 1000 to 500,000 g/mol such as 1000 to 100,000 g/mol, 5000 to 100,000 g/mol or 5000 to 50,000 g/mol. In one embodiment, m is an integer from 5 to 5000; such as from 5 to 4000, such as from 5-3000, such as from 5-2000, preferably from 5 to 1000, more preferably from 20 to 1000 or from 20 to 500. In a preferred embodiment, the molecular weight of the compound of formula (Ib) is in the range of 1000 to 500,000 g/mol such as 1000 to 100,000 g/mol, 5000 to 100,000 g/mol or 5000 to 50,000 g/mol, and wherein m is an integer from 5 to 5000; such as from 5 to 4000, such as from 5-3000, such as from 5-2000, preferably from 5 to 1000, more preferably from 20 to 1000 or from 20 to 500.

In a preferred embodiment, at least two of R₃ are hydroxyl and the remaining R₃ are selected independently from linear or branched C₁-C₆, preferably all the remaining R₃ are methyl. In the most preferred embodiment, two of R₃ are hydroxyl and the remaining R₃ are all unsubstituted methyl.

In a further embodiment, said silanol functional polysiloxane is represented by formula (Ib') below having a molecular weight in the range of 750 to 500,000 g/mol:



wherein (m+m'+m'') is an integer from 5 to 7500; and

wherein (m'+m'') is an integer from 0-50, and

each R3 and each R3' are independently selected from hydroxyl, methyl or linear or branched C₁-C₃₀ alkyl, linear or branched C₂-C₃₀ alkenyl, C₃-C₃₀ cycloalkyl or aryl; R3 is as defined for compound (Ib); with the proviso that at least two R3' groups are hydroxyl groups.

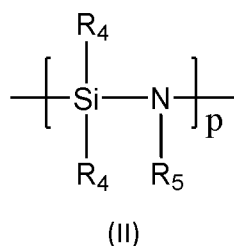
In one embodiment, the molecular weight of the compound of formula (Ib') is in the range of 1000 to 500,000 g/mol, such as 1000 to 100,000 g/mol, 5000 to 100,000 g/mol or 5000 to 50,000 g/mol.

In one embodiment, (m+m'+m'') is an integer from 5 to 5000; such as from 5 to 4000, such as from 5-3000, such as from 5-2000, preferably from 5 to 1000, more preferably from 20 to 1000 or from 20 to 500; and (m'+m'') is an integer from 0-40, such as from 0-30, such as from 0-20, preferably from 0-10.

In the compound of formula (Ib'), in one embodiment at least two R3' are hydroxyl, and the remaining R3' are selected independently from linear or branched C₁-C₆, preferably all the remaining R3' are methyl, and all R3 are selected independently from C₁-C₆ alkyl, preferably all R3 are methyl. In the most preferred embodiment, two R3' are hydroxyl and the remaining R3' and all R3 are all methyl.

In a preferred embodiment, the number of silanol groups in the silanol functional polysiloxane is between 1-100, such as between 1-50, such as between 1-25 or 1-10.

In a preferred embodiment, said one or more polysilazane comprises a compound according to formula (II) below having a linear or branched or cyclic structure:



wherein p is an integer from 5 to 100;

wherein each R4 are independently selected from hydrogen, linear or branched C₁-C₆ alkyl or linear or branched C₁-C₆ alkenyl; and

each R5 are independently selected from hydrogen, linear or branched C₁-C₆ alkyl or linear or branched C₁-C₆ alkenyl;

with the proviso that at least one R4 is not hydrogen.

In one embodiment, p is an integer from 5 to 90, such as from 5 to 80, such as from 5 to 70, such as from 5 to 60, such as from 5-50, such as from 5-40, such as from 5-30, such as from 5-20 or from 10-40.

In one embodiment, at least one of R4 are selected from methyl, ethyl, and vinyl. In one embodiment, at least one of R5 is hydrogen, preferably all R5 are hydrogen.

In a preferred embodiment, the coating composition comprises less than 0.5 parts (weight), such as less than 0.4 parts, such as less than 0.3 parts, such as less than 0.2 parts, such as less than 0.1 parts (weight) inorganic polysilazane relative to 100 parts (weight) of said one or more hydroxyl functional polysiloxane.

In one embodiment, said coating composition further comprises c) one or more catalyst. Preferably, said catalyst c) is present amount between 0.0001-5.0 %, e.g. 0.0001-2.0 %, or 0.005-5 %, or 0.01-4.0 %, or 0.1-3.0 %, by dry weight of the coating composition; or in an amount of 0.0001-0.001%, or 0.0001-0.01% or 0.0001-1.0% by dry weight of the coating composition. In a preferred embodiment, said one or more catalyst comprises an organic amine, such as an amine selected from the list consisting of trimethylamine, triethylamine, tributylamine, 1,5-diazabicyclo [4.3.0] nonene-5 (DBN), 1,8-diazabicyclo [5.4.0] undecene-7 (DBU), 1,1,3,3-tetramethylguanidine, di-methyl amino pyridine (DMAP) and benzotriazole or a benzotriazole derivative. In a preferred embodiment, said one or more catalyst comprises benzotriazole or a benzotriazole derivative.

In one embodiment, the coating composition further comprises one or more components selected from pigments, fillers, additives and solvents. In a further embodiment, the coating composition comprises hydrophobic silica in an amount of 0.5 -20% by dry weight of the coating composition.

In one embodiment, the polysiloxane-based binder system constitutes at least 40 % by dry weight, such as 40-98 % by dry weight, or 45-95 % by dry weight, or 50-95 % by dry weight, preferably 50-90 % by dry weight, or 55-90 % by dry weight, or 60-90 % by dry weight, of the coating composition.

In a preferred embodiment, said coating composition is a fouling release coating composition.

In one aspect, the invention relates to a kit of parts.

In one embodiment, the kit of parts comprises

A) a first container comprising a composition comprising one or more hydroxyl functional polysiloxane as described for the coating composition above; and

B) a second container comprising a composition comprising one or more organic polysilazane as described for the coating composition above;

wherein said kit is for preparation of a coating composition according to the invention.

In a further embodiment, the composition in said first container A) further comprises one or more catalyst as defined for the coating composition above, or said kit further comprises C) a third container comprising one or more catalyst as described for the coating composition above. In one embodiment, the composition in container A) and/or the composition in container B) further comprises one or more further components selected from fillers, pigments, additives and solvents.

In one embodiment, the kit of parts comprises

A) a first container comprising a composition comprising one or more hydroxyl functional polysiloxane as described for the coating composition above, preferably a silanol functional polysiloxane; and one or more organic polysilazane as described for the coating composition above; and

B) a second container comprising one or more catalyst as described for the coating composition above; wherein said kit is for preparation of a coating composition according to the invention.

In a further embodiment, the composition in container A) and/or the composition in container B) further comprises one or more further components selected from fillers, pigments, additives and solvents.

In one aspect, the invention relates to the use of the coating composition according to the invention for application on a substrate such as on a steel substrate, an iron substrate, an aluminum substrate, a bronze substrate or a glass-fiber reinforced polyester substrate. In a preferred embodiment, the surface is the outer surface of a part of a marine structure.

In one aspect, the invention relates to a structure having on at least a part of the outer surface, a cured coat obtained from a coating composition according to the invention. In one embodiment, said structure comprises a marine structure. In a preferred embodiment, said cured coat is a fouling release coat.

In one embodiment, said cured coat has a dry film thickness (dft) in the range of 5-200 μm , such as 10-50 μm or 50-150 μm .

In one embodiment, the structure is having on at least a part of the outer surface a multilayer system comprising

- i) one or more layers of a cured primer;
- ii) one or more layers of cured coat obtained from a coating composition according to the invention; and optionally
- iii) one or more further layers of cured coats not identical to a cured coat obtained from a coating composition according to the invention.

In a further embodiment, iii) said one or more further layers of cured coat comprises one or more layers of fouling release coat.

In a preferred embodiment, said primer is a standard anticorrosive primer.

5 All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference in their entirety and to the same extent as if each reference were independently and specifically indicated to be incorporated by reference and were set forth in its entirety herein (to the maximum extent permitted by law), regardless of any separately provided incorporation of particular documents made elsewhere herein.

10 The use of the terms "a" and "an" and "the" and similar referents in the context of describing the invention are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. For example, the phrase "the composition" is to be understood as referring to various "compositions" of the invention or particular described aspect, unless otherwise indicated.

15 The description herein of any aspect or aspect of the invention using terms such as "comprising", "having," "including" or "containing" with reference to an element or elements is intended to provide support for a similar aspect or aspect of the invention that "consists of", "consists essentially of" or "substantially comprises" that particular element or elements, unless otherwise stated or clearly contradicted by context (e.g., a composition described herein as
20 comprising a particular element should be understood as also describing a composition consisting of that element, unless otherwise stated or clearly contradicted by context).

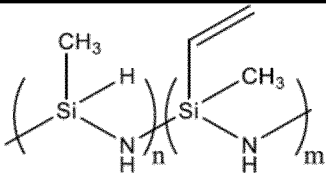
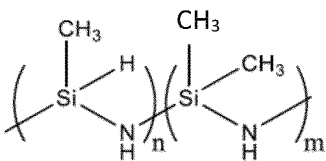
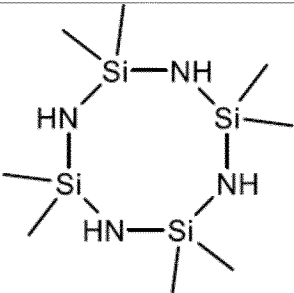
The use of any and all examples, or exemplary language (including "for instance", "for example", "e.g.", and "such as") in the present specification is intended merely to better illuminate the invention, and does not pose a limitation on the scope of invention unless otherwise indicated.

25 Headings and sub-headings are used herein for convenience only, and should not be construed as limiting the invention in any way. The use of any and all examples, or exemplary language (including "for instance", "for example", "e.g.", and "such as") in the present specification is intended merely to better illuminate the invention, and does not pose a limitation on the scope of invention unless otherwise indicated. The citation and incorporation of patent documents herein is
30 done for convenience only, and does not reflect any view of the validity, patentability and/or enforceability of such patent documents.

It should be understood that the various aspects, embodiments, implementations and features of the invention mentioned herein may be claimed separately, or in any combination.

$\text{HO}-\text{Si}\begin{matrix} \text{CH}_3 \\ \\ \text{CH}_3 \end{matrix}-\left(\text{O}-\text{Si}\begin{matrix} \text{CH}_3 \\ \\ \text{CH}_3 \end{matrix}\right)_n-\text{O}-\text{Si}\begin{matrix} \text{CH}_3 \\ \\ \text{CH}_3 \end{matrix}-\text{OH}$	n.a.	C2T ex. Wacker
---	------	----------------

Table 2: Polysilazanes applied in the examples (available from Merck, Germany)

Structure	Trade name
	Durazane 1800
	Durazane 1033
	1,2,3,4,5,6,7,8-octamethylcyclotetrasilazane

Pigments, fillers and solvents applied in the compositions are listed below:

5 Pigments: Carbon black, Titanium dioxide, Iron oxide.

Fillers: Calcium carbonate, Hydrophobic silica (HDK H2000 ex. Wacker), Hydrophilic silica (Aerosil A200 ex. Evonik)

Solvents: Xylene, Butyl Acetate.

Catalysts :

10 Benzotriazole, ex. Merck

Triethylamine, ex. Merck

Diethylaminepropylamine, ex. Merck

Dimethylaminepropylamine, ex. Merck

Diethylaminopyridine, ex. Merck

15 Diazabicyclo(5,4,0)undec-7-ene, ex. Merck

1-ethyl-1H-imidazole, ex. Merck

1-methyl-1H-benzo(d)(1,2,3)triazole, ex. Merck

4,N,N trimethylaniline, ex. Merck

Hexylamine, ex. Merck

Pyridine, ex. Merck

Propylamine, ex. Merck

5 2-erhylimidiazole, ex. Merck

Zinc carboxylate, K-Kat 670, ex. King Industries, Inc.

Acetic acid glacial, ex. Merck

Dibutyltin dilaurate, Neostann U-12, ex. Nitto Kasei Co., Ltd.

Silane crosslinker: Pre-hydrolysed TEOS, TES 40 WN, ex. Wacker

10

Comparative coatings:

Silic One tie-coat, 27450-23410, available from Hempel A/S, Denmark

Silic One top-coat, 77450-59151, available from Hempel A/S, Denmark

15 Coatings used as substrates for adhesion testing:

Hempel's Polyenamel, 55102-00010, Acrylic polyurethane, available from Hempel A/S, Denmark

Hempel Light Primer, 45551-12170, Epoxy, available from Hempel A/S, Denmark

Hempatex Hi-Build, 46330-11480, Chlorinated rubber, available from Hempel A/S, Denmark

Hempatex Enamel, 56360-10000, Acrylic, available from Hempel A/S, Denmark

20 Hempel's Silicone Acrylic, 56940-19000, Acrylic modified polysiloxane, available from Hempel A/S, Denmark

Preparation of the pure binder compositions:

Polysiloxanes were speed-mixed with solvent and catalyst for one minute at 3500 rpm. Thereafter

25 polysilazane was mixed in by speed-mixing another 30 seconds.

Preparation of coating compositions:

Polysiloxane, solvent, catalyst, fillers and pigments were speed-mixed at 3500 rpm for 8-10 minutes.

Thereafter polysilazane was mixed in by speed-mixing another 30 seconds.

30

Application of the coatings:

Directly after mixing the coating compositions were applied to the substrate by either a doctor blade (100 – 300 µm) or by brush. Gelation was achieved within hours. Curing took place by leaving the samples at ambient conditions for two days.

Adhesion test:

Samples produced according to preparation of coating compositions were tested using a razor blade and an eraser. A deep cut through the coating to the substrate was made using the razor. Using the eraser with moderate force the cut in the coating was rubbed perpendicular to the direction of the cut. Visual inspection of the coating showed if the coating break is adhesive (interphase between substrate and cured coat) or cohesive (within the cured coat). The adhesive properties of coating was assessed on scale from 1 – 5 according to table 3 below, results are listed in table 4.

Table 3: Evaluation scale for adhesive properties

Grade	Description
1	The coating is lifted from the substrate in big patches
2	Detachment between the two layers where pressure is exerted
3	Detachment develops slowly from the scribe when pressure is exerted
4	Detachment only occurs in very small areas next to the scribe
5	No detachment between the coats. Only cohesive breakdown.

Table 4a: Adhesion to various substrates.

Composition		Ex. 6	Ex. 7	Silic One tiecoat (comparative)	Silic One topcoat (comparative)
Polysiloxane (g)	Silmer OHT Di-400	2.01	2.01		
Polysilazane (g)	Durazane 1800	0.12	0.125		
Solvent (g)	Butyl acetate	0.5	0.5		
Filler (g)	CaCO ₃		0.5		
Pigment (g)	TiO ₂		0.5		
	FeOOH		0.15		
Catalyst (g)	Benzotriazole	0.00045	0.00045		
Adhesion test	Acrylic	2	2	1	1
	Bronze	5	5	1	1
	Glass	5	5	5	1
	Poly (ethylene terephthalate) (PET)		5	1	1
	Polypropylene (PP)		5	1	1
	Steel	2	5	2	1
	Fresh epoxy	5	5	5	

Table 4a illustrates that the silazane content in the polysiloxane promotes adhesion to various substrates when compared to existing commercially available silicone tiecoat and topcoat.

Table 4b: Adhesion of various compositions to various substrates, including different coating types

Component		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Comparative 1	Comparative 2
Polysiloxane (g)	Silmer OHT Di-400	60	60					
	Silmer OH Di-400			60	45			
	Silmer OH C50				15			
	C2T					60	60	
Polysilazane (g)	Durazane 1033		3	3				
	Durazane 1800	3			5	3		
Silane (g)	Pre-hydrolysed TEOS						3	
Solvent (g)	Butyl acetate	8	8		8			
	Xylene			6		6	6	
Catalyst (g)	Benzotriazole				0.005			
	K-Kat 670		0.1					
	Dibutyltin dilaurate			0.15		0.2	0.4	
	Acetic acid	0.3						
Silic One tiecoat	Silicone tiecoat							100
Adhesion test results	Hempatex Hi-Build	5	5	5	5	5	1	1
	Hempatex Enamel	5	5	5	5	5	1	1
	Hempel's Silicone Acrylic	5	5	5	5	5	1	1
	Steel	5	5	5	5	5	1	1

Table 4c: Adhesion of various compositions to various substrates, including different coating types

Component		Ex. 1	Ex. 2	Ex. 3	Comparative 1
Polysiloxane (g)	Silmer OHT Di-400	60	60		
	Silmer OH Di-400			60	
	C2T				60
Polysilazane (g)	Durazane 1033		3	3	
	Durazane 1800	3			
Silane (g)	Pre-hydrolysed TEOS				3
Solvent (g)	Butyl acetate	8	8		
	Xylene			6	6
Catalyst (g)	K-Kat 670		0.1		
	DBTL			0.15	0.4
	Acetic acid	0.3			
Adhesion test results	Hempel's Polyenamel	5	5	5	1
	Hempel Light Primer	5	5	5	1
	Bronze	5	5	5	1

Tables 4b and 4c show examples of good adhesion to a variety of coatings and metals, whereas comparative examples, Comp. 1 and Comp. 2, show poor adhesion. This illustrates the beneficial adhesion properties when using a composition of the invention.

5 **Antifouling test:**

Performed at raft at the CoaST Maritime test centre in Hundested, 3390 DK.

Period: 6/5-21 to 23/8-21 Position: Eastbound.

Type: Raft, static exposure (20 cm below waterline, acrylic panels (20 x 10 cm)

10 **Table 5: Evaluation scale for antifouling performance**

Scale for grading the performance of coatings undergoing static antifouling testing	
Score	Fouled area (%)
Excellent	Only slime
Good	Algae + Animals < 10%
Fair	10% < Algae + Animals < 25%
Poor	Algae + Animals > 25%

Antifouling test:

Silicone antifouling benchmarking

- 15 Below compositions were prepared according to the description under preparation of coating compositions. The compositions were applied to acrylic panels. Whereas composition C was applied on top of a panel coated with a silic-one tie-coat formulation, compositions A and B were applied directly to the acrylic panel. The panels were immersed according to the procedure described under antifouling tests. The results are summarized in Table 6 below.

20

Table 6: Antifouling properties

Component		A	B	C (comparative)
Polysiloxane (g)	Silmer OHT Di-400	2.01	2.01	
	C2T			1.82
	Silmer TMS Di-10			0.18

Polysilazane (g)	Durazane 1800	0.12	0.125	
Solvent (g)	Butyl acetate	0.5	0.5	
Filler (g)	CaCO ₃		0.5	
Pigment (g)	TiO ₂		0.5	
	FeOOH		0.15	
Catalyst (g)	Benzotriazole	0.00045	0.00045	
	Dibutyltin dilaurate			0.01
Performance on raft in Hundested 35 days		Good	Good	Fair
Performance on raft in Hundested 48 days		Poor	Poor	Poor

Table 6 shows that the antifouling performance of the claimed coating composition is comparable to that of a silicone coating without polysilazane. Hence the novel curing process does not affect the efficacy of the coatings.

5 Drying time:

Drying time for the compositions was measured according to ASTM D5895-20.

Effect of catalyst

Composition D presented below was prepared following the description under preparation of coating compositions.

10 *Table 7: composition D*

	D
Silmer OHT Di-400 (g)	1.00
Durazane 1800 (g)	0.05
Xylene (g)	0.5

Catalysts in different levels were added to composition D and the drying time (hours) was recorded.

The results are shown in table 8a

Table 8a: drying time with various catalysts

	Amount of catalyst added			
	150 ppm*	1200 ppm	3000 ppm	6000 ppm
Catalyst	Stage III (h)	Stage III (h)	Stage III (h)	Stage III (h)
Benzotriazole	1.1	0.2		
Triethylamine		20.8	17.5	
Diethylaminepropylamine		14.4	1.9	
Dimethylaminepropylamine			13.2	12
Dimethylaminopyridine		7.2	1.8	
Diazabicyclo(5,4,0)undec-7-ene	3.6	1.1		
1-ethyl-1H-imidazole			6.4	
1-methyl-1H-benzo(d)(1,2,3)triazole			22.2	15.6
4,N,N trimethylaniline			12.9	

Hexylamine		17.6	1.3	
Pyridine		22.5	16.9	13.9
Propylamine		18.5	5.5	
2-ethylimidazole		3.2	1.5	
No catalyst	21	21	21	21

*ppm: weight ppm relative to composition D

Table 8a shows that it is possible to adjust the curing speed by varying the type and amount of catalyst and thereby obtain a curable composition that can meet various demands.

Table 8b: Drying time with various types of catalysts using different compositions of polysiloxane and polysilazanes

Component		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Polysiloxane (g)	Silmer OHT Di-400	60	60			
	Silmer OH Di-400			60	45	
	Silmer OH C50				15	
	C2T					60
Polysilazane (g)	Durazane 1033		3	3		
	Durazane 1800	3			5	3
Solvent (g)	Butyl acetate	8	8		8	
	Xylene			6		6
Catalyst (g)	Benzotriazole				0.005	
	K-Kat 670		0.1			
	Dibutyltin dilaurate			0.15		0.2
	Acetic acid	0.3				
Drying time	Stage III (h)	1.5	8	3.5	1.75	2.25

Table 8b shows examples with combinations of different binder systems catalyzed by various types of catalysts, here exemplified by using base, acid and metal catalysts.

Observation of curing:

- 10 Tables 9a-9g illustrates a variety of coating compositions falling within the scope of the invention. The coating compositions follow the general preparation of pure binder and coating compositions previously described. Curing after 24 hours (yes/no) was evaluated by inspecting the films visually and by touch. A yes was given to coherent films, a no as given to compositions still in a liquid or viscous state.

15

Table 9a: exemplified coating compositions

Component		E	F	G	H	I	J	K	L
Polysiloxane (g)	Silmer OHT Di-400	3.05	3.025	3.045	3.02	2.131	2.121		

	Silmer OHT E13					0.0734			
	Silmer OH C50						1.206	0.54	0.54
	DMS-C21							0.45	0.45
Polysilazane (g)	Durazane 1800	0.084	0.151	0.3	0.454	0.126	0.169	0.03	0.05
Solvent (g)	Xylene							0.5	0.5
Catalyst (g)	Benzotriazole								
Cured within 24 hours	Y/N	Y	Y	Y	Y	Y	Y	Y	Y

Table 9b: exemplified coating compositions

Component		M	N	O	P	Q	R	S	T
Polysiloxane (g)	Silmer OHT Di-400		1.0	1.0	1.0	1.0	1.0		
	Silmer OH C50	0.54							
	DMS-C21	0.45							
	DMS-S21							1.01	1.03
Polysilazane (g)	Durazane 1800	0.07	0.25	0.05	0.1	0.15	0.15		
Solvent (g)	Xylene	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Catalyst (g)	Benzotriazole							0.00 015	0.00 045
Cured within 24 hours	Y/N	Y	Y	Y	Y	Y	Y	Y	Y

Tables 9a and 9b shows that the various hydroxyl functional siloxane polymers can be used to obtain the curable polysiloxane composition of this invention.

5

Table 9c: exemplified coating compositions

Component		U	V	X	Y	Z	AA	AB
Polysiloxane (g)	Silmer OHT Di-400	1.04	1.05	1.02	1.01	1.02	1.06	1.04
Polysilazane (g)	Durazane 1800	0.06	0.06	0.06	0.06	0.05	0.05	0.05
Solvent (g)	Xylene	0.31	0.45	0.3	0.3	4.81		0.9
	Butyl acetate						4.22	
Filler (g)	CaCO ₃				0.339			
	Hydrophilic silica							0.4
	Hydrophobic silica					0.4	0.4	
Pigment (g)	TiO ₂			0.197	0.237	0.25	0.23	0.24
	Fe ₂ O ₃	0.192			0.063			
	FeOOH					0.067	0.061	0.059
	Carbon black		0.11					
Cured within 24 hours	Y/N	Y	Y	Y	Y	Y	Y	Y

Table 9d: exemplified coating compositions

Component		AC	AD	AE	AF	AG	AH
Polysiloxane (g)	Silmer OHT Di-400	1.01	1.01	1.04	1	1	1
Polysilazane (g)	Durazane 1800	0.05	0.05	0.05	0.06	0.06	0.06
Solvent (g)	Xylene		0.3				
	Butyl acetate	1.7		0.3	0.6	0.5	0.4
Filler (g)	CaCO ₃		0.39	0.42			
	Hydrophilic silica	0.399			0.1	0.2	0.3
Pigment (g)	TiO ₂	0.25	0.28	0.24	0.2	0.2	0.2
	FeOOH	0.066	0.061	0.061	0.06	0.06	0.06
Cured within 24 hours	Y/N	Y	Y	Y	Y	Y	Y

Table 9e: exemplified coating compositions

Component		AI	AJ	AK	AL	AM	AN	AO
Polysiloxane (g)	Silmer OHT Di-400	1	1	1	1	1	1	2
Polysilazane (g)	Durazane 1800	0.06	0.06	0.06	0.06	0.06	0.06	0.1
Solvent(g)	Xylene							1
	Butyl acetate	0.6	0.5	0.4	0.6	0.5	0.4	
Catalyst (g)	Benzotriazole							0.0003
Filler (g)	CaCO ₃				0.1	0.2	0.3	
	Hydrophobic silica	0.1	0.2	0.3				0.02
Pigment (g)	TiO ₂	0.2	0.2	0.2	0.2	0.2	0.2	
	FeOOH	0.06	0.06	0.06	0.06	0.06	0.06	
	Carbon black							0.01
Cured within 24 hours	Y/N	Y	Y	Y	Y	Y	Y	Y

5 Table 9f: exemplified coating compositions

Component		AP	AR	AS	AT	AU	AV
Polysiloxane (g)	Silmer OHT Di-400	2	2	2	2	2	2
Polysilazane (g)	Durazane 1800	0.2	0.3	0.1	0.2	0.3	0.1
Solvent (g)	Xylene	1	1	1	1	1	1
Catalyst (g)	Benzotriazole	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003
Filler (g)	Hydrophilic silica			0.07	0.07	0.07	
	Hydrophobic silica	0.02	0.02				
Pigment (g)	Carbon black	0.01	0.01	0.01	0.01	0.01	0.01
Cured within 24 hours	Y/N	Y	Y	Y	Y	Y	Y

Tables 9c, 9d, 9e 9f show that multiple variations in common coating ingredients that can be used without compromising the curable polysiloxane-based composition.

Table 9g: Comparison of polysilazanes

Component		BB	BC
Polysiloxane (g)	Silmer OH C50	2	2
	DMS-C21	1.68	1.68
Polysilazane (g)	Durazane 1800		0.168
	1,2,3,4,5,6,7,8-OCTAMETHYLCYCLOTETRASILAZANE	0.17	
Solvent (g)	Xylene	1.5	1
Catalyst (g)	Benzotriazole	0.00045	0.00045
Cured withing 24 hours	Y/N	Y	Y

Table 9g shows that various polysilazanes can be used to obtain a curable polysiloxane composition containing polysilazane.

5 **Stability of mechanical properties (rheology measurements):**

Samples were prepared according to the description under preparation of coating compositions.

Samples were cured at ambient conditions in a Teflon mould (size) and cut in 25 mm discs of approximately 500 μ m thickness. Measurements was obtained on a TA Instruments Discovery HR-1 Hybrid Rheometer with a 25 mm parallel steel plate geometry on a Peltier temperature controlled plate. Temperature was set for 25 °C and gap was software controlled to a constant axial force of 3 N. LVE region was determined with a strain sweep at 2.5 Hz between 0.1 to 10%. Frequency sweep was recorded in a logarithmic sweep between 100 and 0.01 Hz. Strain was set at 2.5% for softer samples and 0.5% for harder samples.

The compositions and the storage moduli before and after post curing of the four samples at 180°C for one hour are shown in table 10 below.

Table 10: Storage modulus for various compositions

Component		AX	AY	AZ (comparative)	BA (comparative)
Polysiloxane (g)	Silmer OHT Di-400	7.3	7.3	7.3	6.0
Polysilazane (g)	Durazane 1800	0.3	0.6	0.9	3.6
Solvent (g)	Xylene	3.65	3.65	3.65	3.0
Catalyst (g)	Benzotriazole	0.0005	0.0005	0.0005	0.002
Parts polysilazane per 100 parts polysiloxane (weight)		4.1	8.2	12.3	60
Storage modulus G' (Pa)	Before heating	15008	15513	19891	39209
	After heating	17830	25253	46196	194312
	Increase (%)	19	63	132	396

Table 10 shows that storage modulus of the compositions becomes increasingly unstable with increasing amount of polysilazane. Thus the formulations with low amounts of polysilazanes are more flexible and more stable.

CLAIMS

1. A coating composition comprising a polysiloxane based binder system, wherein said binder system comprises

a) one or more hydroxyl functional polysiloxane; and

5 b) one or more organic polysilazane;

wherein said one or more organic polysilazane constitutes 0.5-10 parts (weight) relative to 100 parts (weight) of said one or more hydroxyl functional polysiloxane.

2. The coating composition according to claim 1, wherein said one or more organic polysilazane constitutes 1-10 parts (weight), such as 2-10 parts (weight), such as 3-10 parts (weight), such as 4-10 parts (weight), such as 5-10 parts (weight), such as 6-10 parts (weight), such as 7-10 parts (weight), such as 8-10 parts (weight), such as 9-10 parts (weight), or 0.5-9 parts (weight), such as 0.5-8 parts (weight), or 0.5-7 parts (weight), or 1-9 parts (weight), or 1-8 parts (weight), or 1-7 parts (weight) or 2-9 parts (weight), preferably 2-8 parts (weight), or 2-7 parts (weight) relative to 100 parts (weight) of said one or more hydroxyl functional polysiloxane.

15

3. The coating composition according to any of claims 1-2, wherein said one or more hydroxyl functional polysiloxane comprises

a1) one or more carbinol functional polysiloxane, and/or

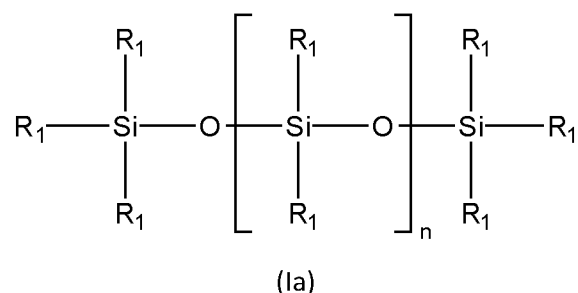
a2) one or more silanol functional polysiloxane.

20

4. The coating composition according to any of claims 1-3, wherein said one or more hydroxyl functional polysiloxane comprises

a1) one or more carbinol functional polysiloxane.

25 5. The coating composition according to any of claims 3-4, wherein said carbinol functional polysiloxane is represented by formula (Ia) below having a molecular weight in the range of 750 to 500,000 g/mol:



30 wherein n is an integer from 5 to 7500; and

wherein each R1 are independently selected from

methyl; or

a 2-30-membered linear or branched saturated or unsaturated chain consisting of carbon atoms and optionally containing one or more linkers selected independently from -O-, -S-, -N-, -N-C(O)-, -O-C(O)-, -N-C(O)-N- and -N-C(O)-O-; or

- 5 a 3-30-membered saturated or unsaturated ring system consisting of carbon atoms and optionally containing one or more linkers selected independently from -O-, -S-, -N-, -N-C(O)-, -O-C(O)-, -N-C(O)-N- and -N-C(O)-O-; or

an aromatic or heteroaromatic ring system;

wherein each R1 may optionally be substituted one or more times with one or more substituents

- 10 selected from halogen, hydroxyl, oxo and R2;

wherein each R2 are independently selected from

methyl; or

a 2-30-membered linear or branched saturated or unsaturated chain consisting of carbon atoms and optionally containing one or more linkers selected independently from -O-, -S-, -N-, -N-C(O)-, -O-C(O)-, -N-C(O)-N- and -N-C(O)-O-; or

- 15 a 3-30-membered saturated or unsaturated ring system consisting of carbon atoms and optionally containing one or more linkers selected independently from -O-, -S-, -N-, -N-C(O)-, -O-C(O)-, -N-C(O)-N- and -N-C(O)-O-; or

an aromatic or heteroaromatic ring system;

- 20 wherein said R2 may optionally be substituted one or more times with halogen, hydroxyl and oxo; and

wherein each optionally substituted R1 is having a Mw of <500 g/mol;

with the proviso that at least one R1 and/or R2 has at least one carbinol functional group.

- 25 6. The coating composition according to claim 5, wherein the molecular weight of the compound of formula (Ia) is in the range of 1000 to 500,000 g/mol, such as 1000 to 100,000 g/mol, 5000 to 100,000 g/mol or 5000 to 50,000 g/mol, and wherein each optionally substituted R1 is having a Mw of <450 g/mol, such as <400 g/mol, such as <350 g/mol, such as <300 g/mol; and wherein n is an integer from 5 to 5000; such as from 5 to 4000, such as from 5-3000, such as from 5-2000, preferably from 5 to 1000, more preferably from 20 to 1000 or from 20 to 500.
- 30

7. The coating composition according to any of claims 5-6, wherein each R1 is independently selected from unsubstituted methyl or an unsubstituted 2-10 membered linear or branched

saturated or unsaturated chain consisting of carbon atoms and optionally containing one or more linkers selected independently from -O-, -S-, -N-C(O)-, -C-O-C(O)- and -N-C(O)-O-.

8. The coating composition according to any of claims 5-7, wherein

- 5 at least two of R1 and/or R2 are having at least one carbinol functional group; or
 at least three of R1 and/or R2 are having at least one carbinol functional group; or
 at least one of R1 and/or R2 is having at least two carbinol functional groups; or
 at least one of R1 and/or R2 are having at least three carbinol functional groups; or
 at least two of R1 and/or R2 are having at least two carbinol functional groups.

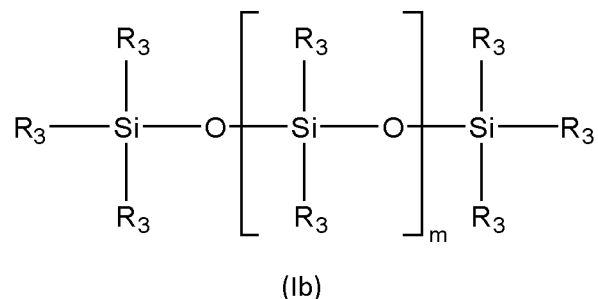
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9. The coating composition according to any of claims 3-8, wherein the number of carbinol groups in the carbinol functional polysiloxane is between 1-100, such as between 1-50, such as between 1-25 or 1-10.

- 15 10. The coating composition according to any of claims 1-3, wherein said one or more hydroxyl functional polysiloxane comprises
 a2) one or more silanol functional polysiloxane.

11. The coating composition according to any of claims 3 and 10, wherein said silanol

- 20 functional polysiloxane is represented by formula (Ib) below having a molecular weight in the range of 750 to 500,000 g/mol:



- 25 wherein m is an integer from 5 to 7500;

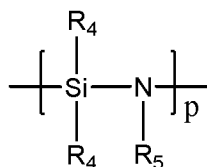
wherein each R3 are independently selected from hydroxyl, methyl or linear or branched C₁-C₃₀ alkyl, linear or branched C₂-C₃₀ alkenyl, C₃-C₃₀ cycloalkyl or aryl;
 with the proviso that at least two R3 groups are hydroxyl groups.

- 30 12. The coating composition according to claim 11, wherein the molecular weight of the compound of formula (Ib) is in the range of 1000 to 500,000 g/mol such as 1000 to 100,000 g/mol,

5000 to 100,000 g/mol or 5000 to 50,000 g/mol, and wherein m is an integer from 5 to 5000; such as from 5 to 4000, such as from 5-3000, such as from 5-2000, preferably from 5 to 1000, more preferably from 20 to 1000 or from 20 to 500.

5 13. The coating composition according to any of claims 11-12, wherein at least two of R₃ are hydroxyl and the remaining R₃ are selected independently from linear or branched C₁-C₆, preferably all the remaining R₃ are methyl.

14. The coating composition according to any of claims 1-13, wherein said one or more
10 polysilazane comprises a compound according to formula (II) below having a linear or branched or cyclic structure:



(II)

15 wherein p is an integer from 5 to 100;
wherein each R₄ are independently selected from hydrogen, linear or branched C₁-C₆ alkyl or linear or branched C₁-C₆ alkenyl; and
each R₅ are independently selected from hydrogen, linear or branched C₁-C₆ alkyl or linear or branched C₁-C₆ alkenyl;
20 with the proviso that at least one R₄ is not hydrogen.

15. The coating composition according to any of claims 1-14, further comprising c) one or more catalyst.

25 16. The coating composition according to claim 15, wherein said one or more catalyst comprises an organic amine, such as an amine selected from the list consisting of trimethylamine, triethylamine, tributylamine, 1,5-diazabicyclo [4.3.0] nonene-5 (DBN), 1,8-diazabicyclo [5.4.0] undecene-7 (DBU), 1,1,3,3-tetramethylguanidine, di-methyl amino pyridine (DMAP) and benzotriazole or a benzotriazole derivative.

30

17. The coating composition according to any of claims 1-16, wherein said polysiloxane-based binder system constitutes at least 40 % by dry weight, such as 40-98 % by dry weight, or 45-95 % by

dry weight, or 50-95 % by dry weight, preferably 50-90 % by dry weight, or 55-90 % by dry weight, or 60-90 % by dry weight, of the coating composition.

18. The coating composition according to any of claims 1-17, wherein said coating composition is
5 a fouling release coating composition.

19. A kit of parts comprising

A) a first container comprising a composition comprising one or more hydroxyl functional polysiloxane as described according to any of claims 1-17; and

10 B) a second container comprising a composition comprising one or more organic polysilazane as described according to any of claims 1-17;
wherein said kit is for preparation of a coating composition according to any of claims 1-17.

20. The kit according to claim 19, wherein, the composition in said first container A) further
15 comprises one or more catalyst as described according to any of claims 15-16; or
said kit further comprises C) a third container comprising one or more catalyst as described according to any of claims 15-16.

21. A marine structure having on at least a part of the outer surface, a cured coat obtained from
20 a coating composition according to any of claims 1-17.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2023/051371

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09D183/04 C09D183/16 C08G77/16 C08G77/62
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G C08L C09D

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

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

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 9 935 246 B2 (CREE INC [US]) 3 April 2018 (2018-04-03) table 1 column 8, line 27 -----	1-21



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

10 March 2023

Date of mailing of the international search report

17/03/2023

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2023/051371

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 9935246	B2	03-04-2018	NONE
