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(54) Title: FOULING CONTROL COATING COMPOSITIONS

(57) Abstract: The present application discloses a fouling control cured paint coat comprising a polysiloxane- based binder matrix and one or more biocides, said binder matrix having included as a part thereof hydrophilic oligomer/polymer moieties, wherein the weight ratio between the hydrophilic oligomer/polymer moieties and the one or more biocides is in the range 1:0.02 to :20, and wherein  $\geq 50\%$  of the binder system is polysiloxane parts. The application further discloses a marine structure comprising on at least a part of the outer surface thereof an outermost coating of the cured paint coat. Moreover, the application discloses the use of the combination of one or more polysiloxane components modified with hydrophilic oligomer/polymer moieties and one or more biocides, wherein the weight ratio between the hydrophilic oligomer/polymer moieties and the one or more biocides is in the range 1:0.02 to :20, for improving the antifouling properties of a polysiloxane based coating composition.

## FOULING CONTROL COATING COMPOSITIONS

## FIELD OF THE INVENTION

The present invention relates to novel fouling control coating compositions.

## BACKGROUND OF THE INVENTION

5 Traditionally, silicone formulations rely on physical means, this being mainly a factor of modulus of elasticity and surface tension to create a low bio-fouling surface. The traditional polydimethylsiloxane (PDMS) coatings have shown difficulty in resisting bio-fouling over time, thus decreasing the advantage of drag reduction.

Hence, there is a need for fouling control polysiloxane-based coating compositions combining  
10 the benefits of conventional polysiloxane-based fouling-release coating compositions with the benefits of biocide-based antifouling coating compositions.

WO 2007/053163 discloses an antifouling material that may include one or more of a number of suitable copolymers (e.g. block copolymers, graft copolymers, etc.) which provide biocidal and/or fouling release characteristics. The copolymers may include a polysiloxane backbone  
15 with one or more polymers grafted onto the polysiloxane backbone. Such grafted polymers may carry biocidal groups.

WO 2008/132195 discloses an antifouling coating composition comprising a curable polymer (e.g. an organosiloxane-containing polymer) and an organosilicone polymer.

WO 2008/132196 discloses a method to physically deter marine fouling which method  
20 involves forming on the substrate a coating composition comprising curable polyorganosiloxane, polyoxyalkylene block copolymer, organosilicon cross-linking agent and/or catalyst. The polyoxyalkylene is reacted to the silicone binder by addition reaction (vinyl/hydride) to form a block copolymer of polyoxyalkylene and polysiloxane. The copolymer can subsequently be terminated with vinyltrimethoxysilane to form a moisture  
25 curable binder.

US 2004/006190 discloses a room-temperature curable organopolysiloxane composition, which includes (A) an organopolysiloxane with the terminals blocked with a hydroxyl group, a hydrolysable group, or both these types of groups, and (B) an organosilicon compound

containing a hydrolysable group, a partial hydrolysis-condensation product thereof, or a mixture of the two, and (C) a polysiloxane with at least one oxyalkylene group bonded to a silicon atom via, for example, a C-C-Si linkage.

WO 2002/088043 discloses a process for coating a siliceous substrate with a silicon-

5 containing layer, wherein in a first step a layer comprising a biocide is applied.

US 2002/0197490 A1 discloses a curable antifouling polysiloxane based composition comprising hydrophobic silica possibly in combination with hydrophilic silica. In some embodiments, the composition further comprises a silicone oil, e.g. oils comprising poly(ethylene glycol) or poly(propylene glycol) moieties. It is further envisaged, that

10 antifouling agents may be used, in particular copper and inorganic copper compounds.

EP 2 103 655 A1 discloses a curable antifouling polysiloxane based composition comprising a reaction curable silicone rubber and a particularly designed organopolysiloxane mixture. In some embodiments, the composition further comprises a silicone oil, e.g. a polyether-modified silicone oil. It is further envisaged, that antifouling agents may be used, in

15 particular copper and inorganic copper compounds.

US 6,313,193 B1 i.a. discloses a composition comprising a silanol-terminated polydimethyl siloxane, a dimethylethoxy-terminated polydimethyl siloxane, polydiethoxy siloxane, and benzalkonium chloride. The polydiethoxy siloxane reacts with the polydimethyl siloxanes so that the polydiethoxy siloxane becomes an integral part of the binder network.

20 JP 2006 052283 A discloses a coating composition comprising a polyether-modified silicone oil having polyoxyalkylene side chains, an acrylic type binder system based on a polysiloxane macropolymer and an antifoulant.

JP 2006 299132 A discloses an antifouling coating composition which is based on a vinyl copolymer binder system which include polysiloxane side chains, and which is modified with 25 certain reactive silanes, and which further comprises, e.g., an poly(oxyalkylene)-modified polysiloxane. The composition may also include an antifouling agent.

JP 05-263022 discloses a hydrolysable coating composition typically based on an acid-anhydride vinyl binder for preventing aquatic organism attachment.

EP 1 261 318 A1 discloses a triphenylboron compound-containing antifouling coating

30 composition stabilised with an amine compound. The composition comprises a non-reactive polysiloxane (oil) modified with oxyalkylene groups.

US 2009/0018276 A1 discloses a polysiloxane based coating composition having biocide moieties covalently bound to the binder matrix.

The silicone based fouling release coatings have demonstrated an advantage over conventional antifouling coatings showing significant lower drag resistance, hence reduced  
5 fuel consumption of marine vessels. The difference is especially obvious as long as the silicone coating is free from marine fouling including slime fouling. Many conventional silicone coatings have until now only been able to maintain a slime free surface for a shorter period.

A few biocide containing antifouling coatings have demonstrated a greater resistance towards marine fouling compared to the silicone based fouling release coatings under e.g. static  
10 conditions. The surface characteristics of such a coating will however lead to an increased drag resistance compared to silicone coatings even when the surface is fouling free.

The rationale behind the present invention has been to prolong the slime free period of a silicone based coating by combining the biocidal components from the antifouling coatings with a silicone based fouling release coating. This provides a coating with low drag resistance  
15 that will remain fouling free for a longer time than conventional silicone based fouling release coatings.

## SUMMARY OF THE INVENTION

In view of the above-mentioned needs, the present inventors have now developed paint compositions for preparing new fouling control coatings (i.e. a cured paint coat) comprising  
20 (i) a polysiloxane-based binder matrix having included as a part thereof hydrophilic oligomer/polymer moieties, and (ii) one or more biocides, which matrix facilitates and controls the leaching of the biocides. In this way, the advantages of silicone fouling release are combined with those of traditional anti-fouling coatings, thus gaining a foul-free, low-friction surface with the use of a relatively small amount of biocide.  
25 The present inventors have realised that the use of a polysiloxane-based binder system having included as a part thereof hydrophilic oligomer/polymer moieties, in particular poly(oxyalkylene) moieties, (see further below) renders it possible to obtain a media for water- and biocidal transport through the cured polysiloxane matrix film. The leach rate of the biocide can be controlled amongst others by the amount and the hydrophilicity of the  
30 hydrophilic oligomer/polymer moieties.

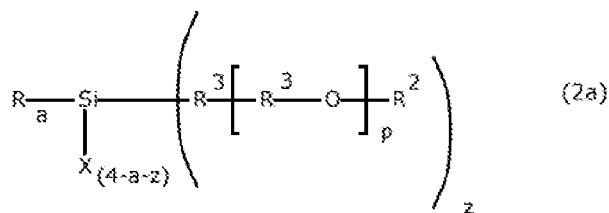
So, in a first aspect the present invention relates to a cured paint coat comprising a polysiloxane-based binder matrix and one or more biocides, said binder matrix having included as a part thereof hydrophilic oligomer/polymer moieties, wherein the weight ratio between the hydrophilic oligomer/polymer moieties and the one or more biocides is in the 5 range 1:0.02 to 1:20, and wherein more than 50 % by weight of the binder matrix is represented by polysiloxane parts.

A second aspect of the invention relates to a marine structure comprising on at least a part of the outer surface thereof a paint coat as defined herein.

In a third aspect the present invention relates to a fouling control coating composition 10 comprising a polysiloxane-based binder system, said binder system comprising one or more polysiloxane components modified with hydrophilic oligomer/polymer moieties, and one or more biocides, wherein the weight ratio between the hydrophilic oligomer/polymer moieties and the one or more biocides is in the range 1:0.02 to 1:20, and wherein more than 50 % by weight of the binder system is represented by polysiloxane parts.

15 In a fourth aspect, the present invention relates to a fouling control coating composition comprising a polysiloxane-based binder system, said binder system comprising one or more hydrophilic oligomer/polymer moieties which at one or both ends carry  $-\text{Si}(\text{R}^*)_3$  groups, wherein each  $\text{R}^*$  independently is selected from  $\text{C}_{1-4}$ -alkyl and  $\text{C}_{1-4}$ -alkoxy, or  $\text{R}^*$  is another condensation curable termination, at least one being  $\text{C}_{1-4}$ -alkoxy, or at least one being 20 another condensation curable termination, and one or more biocides, wherein the weight ratio between the hydrophilic oligomer/polymer moieties and the one or more biocides is in the range 1:0.02 to 1:20, and wherein more than 50 % by weight of the binder system is represented by polysiloxane parts.

A fifth aspect of the invention relates to a fouling control coating composition comprising a 25 polysiloxane-based binder system, said binder system comprising a cross-linker of formula (2a)



wherein, each R represents, independently, an unsubstituted or substituted monovalent hydrocarbon group of 1 to 6 carbon atoms or a hydrolysable group; each X represents, independently, a hydrolysable group; each R<sup>2</sup> is independently selected from -H, C<sub>1-4</sub>-alkyl (e.g. -CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, -CH(CH<sub>3</sub>)<sub>2</sub>, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), phenyl (-C<sub>6</sub>H<sub>5</sub>), and C<sub>1-4</sub>-

5 alkylcarbonyl (e.g. -C(=O)CH<sub>3</sub>, -C(=O)CH<sub>2</sub>CH<sub>3</sub> and -C(=O)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), in particular -H and methyl; each R<sup>3</sup> is independently selected from C<sub>2-5</sub>-alkylene (e.g. -CH<sub>2</sub>CH<sub>2</sub>- , -CH<sub>2</sub>CH(CH<sub>3</sub>)-, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>- , -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>- , -CH<sub>2</sub>CH(CH<sub>2</sub>CH<sub>3</sub>)-), arylene (e.g. 1,4-phenylene) and C<sub>2-5</sub>-alkylene substituted with aryl (e.g. 1-phenyl ethylene), in particular from C<sub>2-5</sub>-alkylene such as -CH<sub>2</sub>CH<sub>2</sub>- and -CH<sub>2</sub>CH(CH<sub>3</sub>)-); p is 0-50; a is 0-2; z is 1-3;

10

and one or more biocides, wherein the weight ratio between the poly(oxyalkylene) and the one or more biocides is in the range 1:0.02 to 1:20, and wherein more than 50 % by weight of the binder system is represented by polysiloxane parts.

15 A sixth aspect of the invention relates to the use of the combination of one or more polysiloxane components modified with hydrophilic oligomer/polymer moieties and one or more biocides, wherein the weight ratio between the hydrophilic oligomer/polymer moieties and the one or more biocides is in the range 1:0.02 to 1:20, for improving the antifouling properties of a polysiloxane based coating composition.

#### DETAILED DISCLOSURE OF THE INVENTION

20 *The cured paint coat*

As mentioned above, the present invention provides a cured paint coat comprising a polysiloxane-based binder matrix and one or more biocides, said binder matrix having included as a part thereof hydrophilic oligomer/polymer moieties, wherein the weight ratio between the hydrophilic oligomer/polymer moieties and the one or more biocides is in the 25 range 1:0.02 to 1:20, such as 1:0.05 to 1:10, and wherein more than 50 % by weight of the binder system is represented by polysiloxane parts.

The paint coat is preferably used as the top coat in a coating system comprising two or more paint coat layers (e.g. at least a primer coat and a tie coat in addition to the top coat).

Without being bound to any particular theory, it is believed that the function of the 30 polysiloxane-based binder matrix rendered hydrophilic by means of oligomer/polymer moieties is to facilitate the transport and accessibility of the biocide at the surface upon contact with sea-water. Potentially, a hydrated layer formed at the coating-water interphase

will also aid in retaining the biocide at the surface, hence allowing the coating to exert its fouling deterrent activity for extended exposure intervals.

It should be understood that the hydrophilic oligomer/polymer moieties forms a part of the polysiloxane-based binder matrix, i.e. that the moieties are covalently incorporated into the 5 binder matrix. It should also be understood that the formed covalent bond(s) preferably are non-hydrolysable.

The polysiloxane-based binder matrix 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, or 10 60-80 % by dry weight, of the cured paint coat.

The term "polysiloxane-based binder matrix" is intended to mean that the binder matrix mainly consists of polysiloxane parts, i.e. that more than 50 % by weight, preferably more than 60 % by weight, e.g. more than 70 % by weight, of the binder matrix is represented by polysiloxane parts. Preferably, the polysiloxane parts constitute 50-99.99 % by weight, e.g.

15 50-99.9 % by weight, in particular 60-99.5 % by weight, or 50-99 % by weight, or 60-98 % by weight, or 70-97 % by weight, or even 70-99 % by weight, or 80-98 % by weight, or 90-97 % by weight, of the binder matrix (i.e. the binder components and any cross-linkers). The remainder of the binder matrix is preferably made of the hydrophilic oligomer/polymer 20 moieties and any (non-polysiloxane-type) cross-linkers. This being said, the hydrophilic oligomer/polymer moieties preferably makes up 1-30 % by weight, such as 2-20 % by weight, e.g. 1-10 % by weight, of the binder matrix.

It should of course be understood that the hydrophilic oligomer/polymer moieties which are included in the polysiloxane-based binder matrix are of non-silicon origin.

When calculating the amount of the polysiloxane parts and the hydrophilic oligomer/polymer 25 moieties, respectively, for a given starting material (or an adduct), it is typically fairly straightforward to distinguish between the two. However, in order to eliminate any doubt about any linkers between the two, it should be understood that the hydrophilic oligomer/polymer moieties include all atoms up to, but not including, the silicon atom which is adjacent to the hydrophilic oligomer/polymer moiety. As an example, in a structure of the 30 type [polysiloxane-O]-Si(Me)<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-[hydrophilic oligomer]-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-Si(Me)<sub>2</sub>-[O-polysiloxane]], the [polysiloxane-O]-Si(Me)<sub>2</sub> parts are accounted for as silicone parts, whereas the CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-[hydrophilic oligomer]-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> moiety is accounted for as the hydrophilic oligomer moiety.

Suitable hydrophilic oligomer/polymer moieties are those selected from poly(vinyl pyrrolidone), poly[N-(2-hydroxypropyl)methacrylamide], poly(N,N- dimethacrylamide), poly(acrylic acid), poly(glycerol), polyHEMA, polysaccharides, poly(vinyl alcohol), polyketones, poly(aldehyde guluronate), polyvinylamine, polycaprolactones, poly(vinyl acetate), polyoxyalkylenes like poly(ethylene glycol), poly(propylene glycol), poly(2-methyl-2-oxazoline), etc., including copolymers of the foregoing. Preferably the hydrophilicity is obtained by modification with polyoxyalkylene moieties like poly(ethylene glycol).

Incorporation of the above mentioned hydrophilic oligomer/polymer into the polysiloxane polymer backbone is typically done through a linking group. The linking group is understood 10 as the product of the reaction of two mutually reaction functional groups; one functional group on the polysiloxane backbone and one on the hydrophilic oligomer/polymer. E.g. an amine linking group is result of for example - but not exclusively - the reaction of a glycidyl ether with a primary or secondary amine. Examples of useful linking groups between the hydrophilic oligomer/polymer and the polysiloxane backbone are: amine groups, ether 15 groups, amide groups, 1,2,3-triazole, C-C bonds, C-C double bonds, C-C triple bonds, Si-C bonds, C-S bonds, S-S bonds, urethane group, urea groups. Most preferred linking group is the Si-C bond prepared by hydrosilylation reaction catalyzed by platinum where the functional group on the polysiloxane backbone is a hydride and the functional group on the hydrophilic oligomer/polymer is an allyl group.

20 In some embodiments, it is preferred that the hydrophilic oligomer/polymer moieties provide a permanent hydrophilic contribution to the binder matrix. Hence, in such embodiments, the hydrophilic oligomer/polymer moieties are preferably devoid of any bonds which are hydrolysable in sea-water. Hence, preferably, the hydrophilic oligomer/polymer moieties do not include ester bonds or acid anhydride bonds.

25 In other embodiments, it is also preferred that the hydrophilic oligomer/polymer moieties provide a permanent hydrophilic contribution to the binder matrix. But, in such embodiments, the link between the hydrophilic oligomer/polymer moieties and the silicone is devoid of any bonds which are hydrolysable in sea-water. Hence, preferably, the hydrophilic oligomer/polymer moieties are not attached to the polysiloxane through hydrolysable bonds 30 such as for example ester bonds or acid anhydride bonds. However, the hydrophilic moiety may in itself include hydrolysable bonds, such as for example an acetate capped poly(oxyalkylene).

In the present context oligomer/polymer moieties are understood as those encompassing at least 3 repeating units, such as at least 5 repeating units. Typically, oligomer/polymer

moieties used for modification include 3-1,000 repeating units, such as 3-200, or 5-150, or 5-100, or 10-80, or 5-20, repeating units.

In some preferred embodiments, the hydrophilic oligomer/polymer moieties (i.e. oligomeric or polymeric groups incorporated into the binder matrix) have a number average molecular weight ( $M_n$ ) in the range of 100-50,000 g/mol, such as in the range of 100-30,000 g/mol, in particular in the range of 150-20,000 g/mol, or in the range of 200-10,000 g/mol.

In the present description with claims, the terms "hydrophilic oligomer/polymer moieties", "hydrophilic polymer moieties", and similar are intended to mean that the oligomeric or polymeric moieties, in themselves (i.e. when represented as discrete molecules) have a solubility of at least 1 % (w/w) in demineralized water at 25°C.

#### *Polysiloxane-based binder system*

The cured paint coat of the invention is typically prepared from a binder system which – upon curing – forms a cross-linked polysiloxane-based binder matrix which incorporates the biocide(s) as well as other constituents such as additives, pigments, fillers, etc. in the cured paint coat.

Hence, it should be understood that the polysiloxane-based binder matrix is made up of reactive polysiloxane binder components, e.g. functional organopolysiloxanes, cross-linkers, silicates (e.g. ethyl silicate), and the like. Thus, it is believed that the reaction between such components will result in the binder matrix in the form of a typically three-dimensional covalently interconnected network.

The cured paint coat may be formed in various ways, e.g. polymerization/cross-linking by formation of siloxane bonds through a condensation reaction or by the use of their reactive groups such as for example amine/epoxy, carbinol/isocyanate etc. Condensation reaction is preferred.

The polysiloxane based binder is a functional organopolysiloxane, with terminal and/or pendant functionality. The terminal functionality is preferred. The functionality can either be hydrolysable groups, such as for example alkoxy groups, ketoxime groups or the functionality can be silanol groups. A minimum of two reactive groups per molecule is preferred. If the molecule contains only two reactive groups, for example silanol groups, it may be necessary to use an additional reactant, a cross-linker, to obtain the desired cross-link density. The cross-linker can for example be an alkoxy silane such as methyltrimethoxysilane, but a wide

range of useful silanes are available as will be described further on. The silane can be used as it is or as hydrolysis-condensation products of same. Although condensation cure is much preferred, the functionality of the organopolysiloxane is not limited to a condensation cure. If so desired, other types of curing can be utilized, for example amine/epoxy either alone or in 5 combination with a condensation reaction. In such cases, the organopolysiloxane can have terminal groups of epoxy or amine and pendant hydrolysable groups, for example with alkoxyfunctionality.

The polysiloxane-based binder system discussed above is characterized by having included therein, as a part of the binder matrix, one or more polysiloxane components which are 10 modified with hydrophilic oligomer/polymer moieties. Hence, such polysiloxane components will upon reaction with other polysiloxane components and cross-linkers provide hydrophilic properties to the binder system. Alternatively, hydrophilic oligomer/polymer moieties functionalized with reactive silanes which enable them to react with the polysiloxane binder, or the hydrophilic oligomer/polymer moieties, and form a non-hydrolysable bond, may also 15 be used.

The polysiloxane components must include silicon-reactive groups such as Si-OH groups, hydrolysable groups such as Si-OR (such as alkoxy, oxime, acetoxy etc.) groups, etc., so as to facilitate reaction with other constituents of the polysiloxane-based binder system.

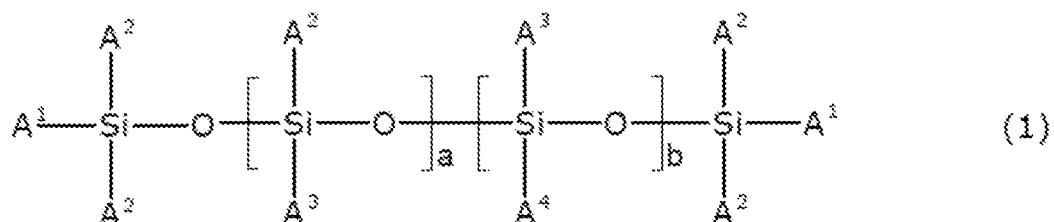
In one currently preferred embodiment of the above, the hydrophilic oligomer/polymer 20 moiety is a poly(oxyalkylene) moiety.

In some embodiments, the fouling control coating composition including the polysiloxane-based binder system may be a reaction-curable composition or a condensation-curable composition as will be evident for the person skilled in the art. Examples hereof are a two-component condensation curing composition based on a silanol-reactive polydiorganosiloxane 25 and a silane with hydrolysable groups, or a one-component condensation-curable composition based on a polydiorganosiloxane with alkoxy or other hydrolysable reactivity. Another example is a reaction curable composition based on an epoxy-functional polysiloxane binder and an amine functional polysiloxane curing agent. Combinations of reaction-curable compositions and condensation-curable compositions are possible, if the binder or the curing 30 agent (or both) includes condensation curable groups, such as alkoxy groups.

In one embodiment, the binder phase comprises (i) a binder and (ii) a cross-linking agent of which the binder (i) should include hydrolysable groups or other reactive groups so as to participate in the formation of the matrix.

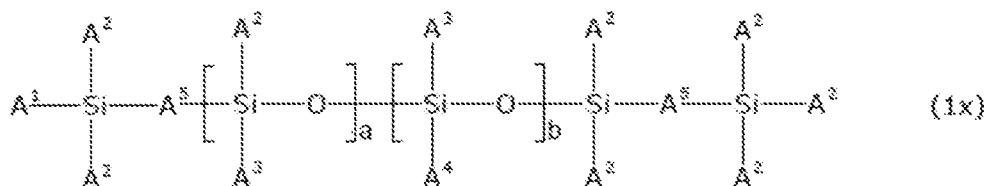
The binder (i) typically constitutes 20-90 % by dry weight of the coating composition, and it should be understood, that the binder (i) may be of different types, e.g. two or more of the types described above, so that the binder (i) may, for example, comprise a non-modified curable polysiloxane and a curable polysiloxane which has been modified with hydrophilic 5 moieties.

In one embodiment, the binder includes a curable diorganopolysiloxane represented by a general formula (1) shown below:



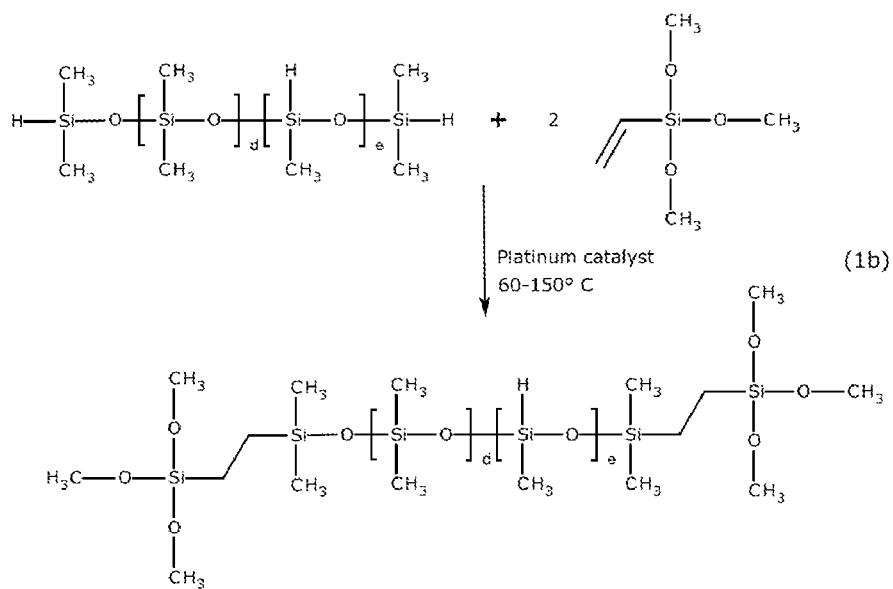
10 wherein each  $\text{A}^1$  is independently selected from a hydroxyl group, a hydrolysable group and another functional group, such as amine or epoxy; each  $\text{A}^2$  is independently selected from alkyl, aryl, alkenyl and a hydrolysable group; each  $\text{A}^3$  and  $\text{A}^4$  is independently selected from alkyl, aryl alkenyl and a hydrophilic group, such as a polyoxyalkylene group, wherein, if  $\text{A}^3$  and/or  $\text{A}^4$  is a hydrophilic group, such as a polyoxyalkylene group, such group may be 15 attached to the silicon atom via a  $\text{C}_{2-5}$ -alkylene linker;  $a = 1-25,000$ ,  $b = 1-2,500$  and  $a+b$  is at least 5.

In one alternative embodiment, the binder includes a curable diorganopolysiloxane represented by a general formula (1x) shown below:



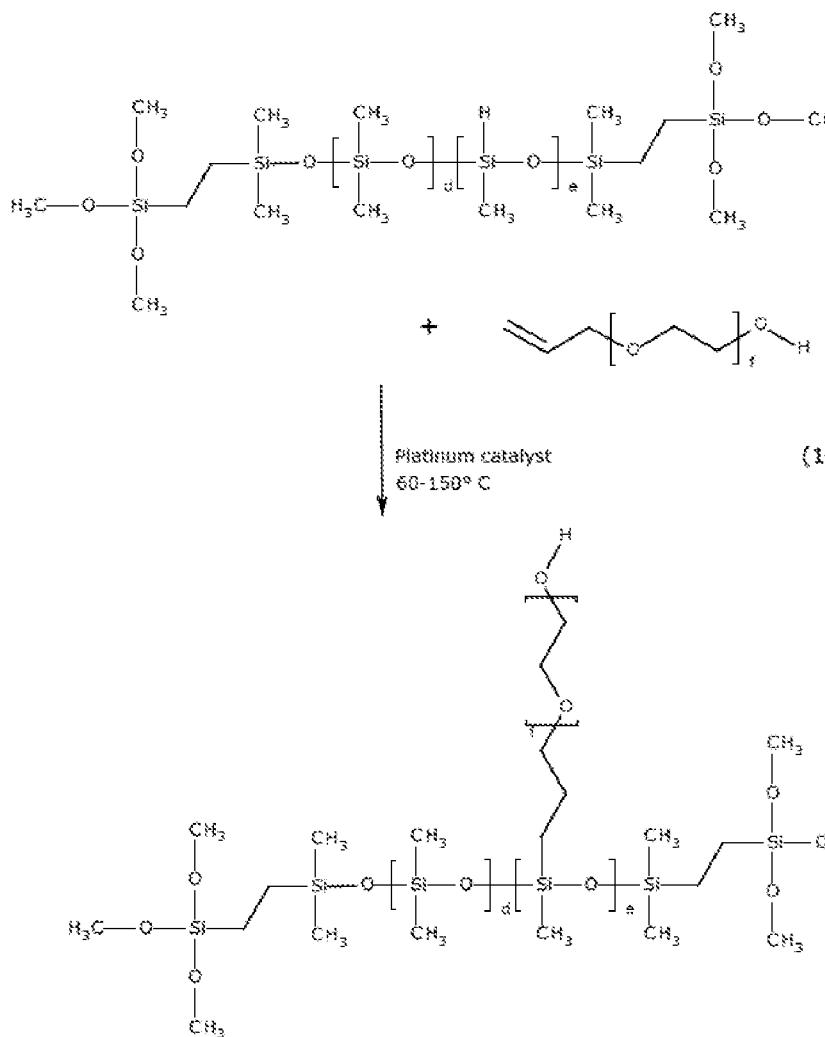
wherein each of  $A^1$ ,  $A^2$ ,  $A^3$ ,  $A^4$ ,  $a$  and  $b$  are as above for formula (1) and wherein each  $A^5$  is independently selected from oxygen or an alkyl group of 2-5 carbon atoms.

In another embodiment, the polysiloxane binder has hydrophilic oligomer/polymer moieties grafted as side chains (pendant hydrophilic groups), as depicted below, and can be prepared 5 by a hydrosilylation reaction between a hydride functional polysiloxane and a hydrophilic component containing an unsaturated group (-CH=CH<sub>2</sub>) such as for example an allyl or vinyl group, in presence of a hydrosilylation catalyst, such as platinum, in accordance with formula (1c), where the example of a hydrophilic compound is an allyl-terminated poly(ethylene glycol). The synthesis is carried out at elevated temperatures, such as 60-150°C. To render 10 the polymer curable, it is necessary to functionalise it with a hydrolysable, or by other means reactive, group, such as vinyltrimethoxysilane. The reaction is following same principles as when grafting the hydrophilic compound to the polysiloxane, and it is outlined in formula (1b), and the functionalization may be done, but not necessarily, prior to the bonding of a hydrophilic group.



15

The resulting binder from the reaction (1b) is further modified with a hydrophilic component, for example poly(ethylene glycol) mono allyl ether as outlined in formula (1c) resulting in a curable, polysiloxane modified with hydrophilic oligomer/polymer moieties.



The binder obtained can be used as is, or in combination with a curable diorganosiloxane (of the generic type presented in formula (1)). As previously described, hydrophilic polymers other than poly(ethylene glycol) are also useful for rendering the polysiloxane hydrophilic.

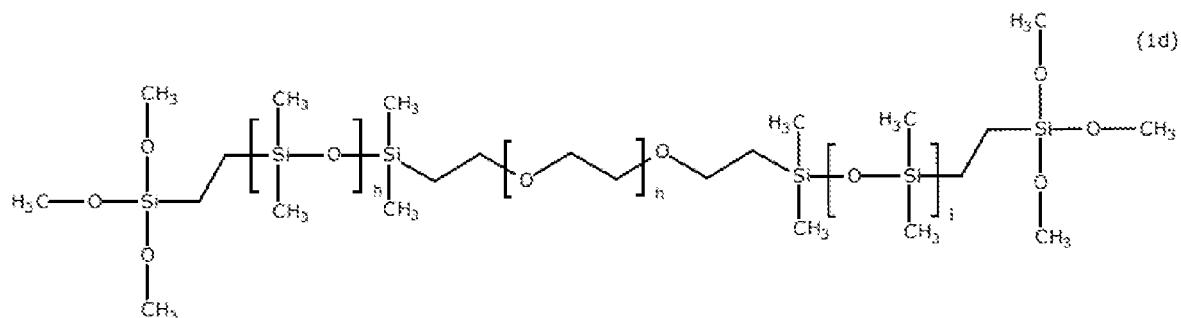
5 It is possible to graft the hydrophilic pendant moieties to the polysiloxane prior to grafting the hydrolysable silane to the polysiloxane (i.e. in reverse order than the synthesis described in formulae (1b) and (1c)).

Hence, in one interesting embodiment, the cured paint coat comprising a polysiloxane-based binder matrix has included as a part thereof pendant hydrophilic oligomer/polymer moieties.

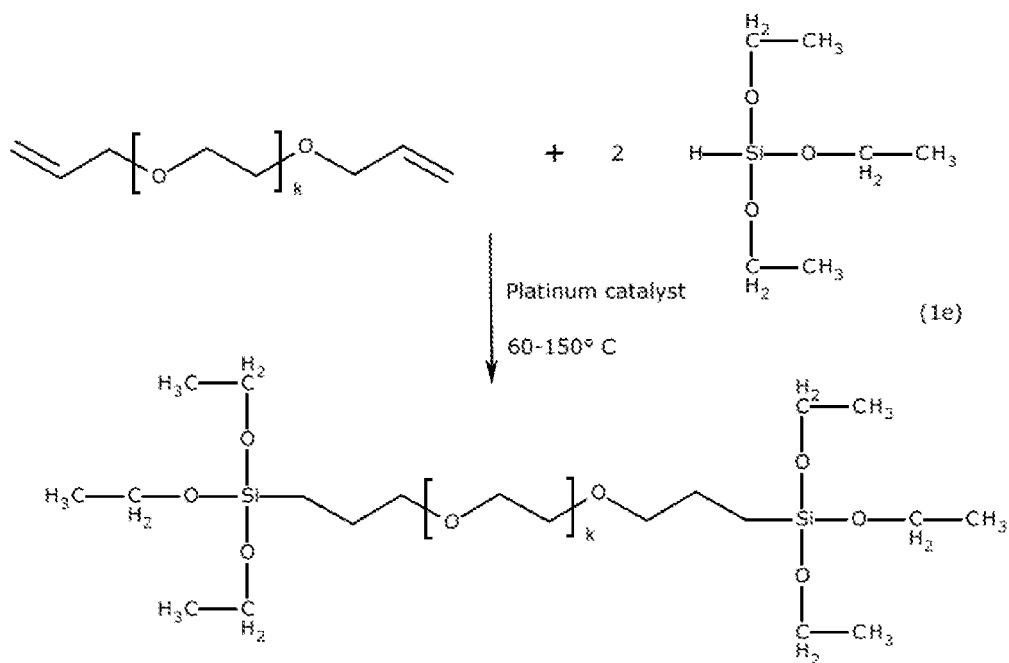
10 The expression “pendant” means that the hydrophilic oligomer/polymer moieties are attached to the polysiloxane backbone at a non-terminal position and that such moieties are attached at only the one end so that the pendant hydrophilic oligomer/polymer forms a “graft” to the polysiloxane backbone (matrix).

Pendant hydrophilic oligomers/polymer moieties may in principle carry functional (non-reactive) groups at the free end, e.g. groups exhibiting a biocidal effect, etc. However, in most embodiments, the hydrophilic oligomers/polymer moieties are not carrying such functional groups, but are in the form of the native oligomer/polymer, possibly end-capped, 5 like with an alkyl group, or possibly with a hydroxyl group or methoxy terminated.

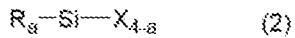
Another variation of the binder is an A-B-A copolymer of polysiloxane (A) and a hydrophilic polymer (B), such as poly(oxyalkylene). An example of the structure of the polymer is depicted in formula (1d). In this variation, units of a polymer with hydrophilic character, such as polyoxyalkylene are introduced in the backbone of the polysiloxane to form an alternating 10 block copolymer. Introducing hydrophilic groups such as oxyalkylene groups in the binder may increase the hydrophilicity of the binder as described in reference WO 2008/132196. The binders can be used alone or in combination, and the structure of the copolymer can be A-B-A and B-A-B. In case of B-A-B, a pendant curable functionality is required, since the terminal groups of the silicone portion would be blocked by the hydrophilic polymer.



In yet another variant, the hydrophilic component is obtained by hydrosilylation of a polyoxyalkylene compound containing at least one, unsaturated group (-CH=CH<sub>2</sub>) such as an allyl or a vinyl group, with a silane having a hydride group, e.g. HSi(R\*)<sub>3</sub> groups, wherein 20 each R\* independently is selected from C<sub>1-4</sub>-alkyl and C<sub>1-4</sub>-alkoxy (e.g. methyl, ethyl, propyl, butyl, methoxy, ethoxy, propoxy, and butoxy), at least one being C<sub>1-4</sub>-alkoxy, such as for example trimethoxysilane, triethoxysilane or methyldimethoxysilane, in the presence of a hydrosilylation catalyst, such as platinum, yielding a curable poly(oxyalkylene). The reaction is carried out at elevated temperatures, such as 60-150°C. The synthesis is outlined in formula (1e). The polymer has to be used in combination with, e.g., component (i) (formula 25 (1)). Further examples of useful silanes include, without being limited to, triethoxysilane, tripropoxysilane, tert-butyldiethoxysilane.



The cross-linking agent (ii) preferably constitutes 0-10 % by dry weight of the coating composition and is, e.g., an organosilicon compound represented by the general formula (2) shown below, a partial hydrolysis-condensation product thereof, or a mixture of the two:



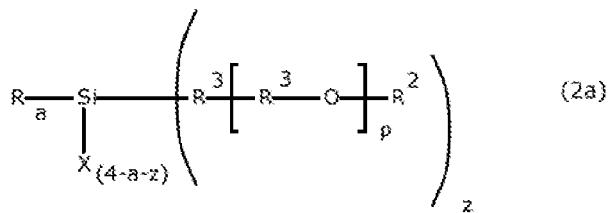
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wherein, each R represents, independently, an unsubstituted or substituted monovalent hydrocarbon group of 1 to 6 carbon atoms or a hydrolysable group, each X represents, independently, a hydrolysable group, and a represents an integer from 0 to 2, such as from 0 to 1.

- 10 The compound outlined in formula (2) acts as a cross-linker for the binder (i). The composition can be formulated as a one component curable RTV (room-temperature vulcanizable) by admixing the binder (i) and the cross-linking agent (ii). If the reactivity on the terminal Si-group of the binder (i) consist of readily hydrolysable groups, such as dimethoxy or trimethoxy, a separate cross-linker is usually not necessary to cure the film.
- 15 The technology behind the curing mechanism and examples of cross-linkers is described in prior art (US 2004/006190).

In one embodiment, R represents a hydrophilic group such as a poly(oxyalkylene). In this case, it is preferred to have a  $\text{C}_{2-5}$ -alkyl spacer between the Si-atom and the polyoxyalkylene group. Hence, the organopolysiloxane may have oxyalkylene domains.

In one variant, the hydrophilicity may be obtained (or added to the hydrophilicity which may have been obtained by incorporating a hydrophilic group to component (i) as outlined in previous section), by using a hydrophilic silane, such as the generic type expressed in formula (2a). The hydrophilic silane will react with the silanol or the hydrolysable groups in 5 the binder component (formula (1) or (1e)), and thereby incorporate a hydrophilic component.



wherein, each R represents, independently, an unsubstituted or substituted monovalent hydrocarbon group of 1 to 6 carbon atoms or a hydrolysable group; each X represents, 10 independently, a hydrolysable group; each  $R^2$  is independently selected from -H,  $C_{1-4}$ -alkyl (e.g.  $-CH_3$ ,  $-CH_2CH_3$ ,  $-CH_2CH_2CH_3$ ,  $-CH(CH_3)_2$ ,  $-CH_2CH_2CH_2CH_3$ ), phenyl ( $-C_6H_5$ ), and  $C_{1-4}$ -alkylcarbonyl (e.g.  $-C(=O)CH_3$ ,  $-C(=O)CH_2CH_3$  and  $-C(=O)CH_2CH_2CH_3$ ), in particular -H and methyl; each  $R^3$  is independently selected from  $C_{2-5}$ -alkylene (e.g.  $-CH_2CH_2-$ ,  $-CH_2CH(CH_3)-$ ,  $-CH_2CH_2CH_2-$ ,  $-CH_2CH_2CH_2CH_2-$ ,  $-CH_2CH(CH_2CH_3)-$ ), arylene (e.g. 1,4-phenylene) and  $C_{2-5}$ -15 alkylene substituted with aryl (e.g. 1-phenyl ethylene), in particular from  $C_{2-5}$ -alkylene such as  $-CH_2CH_2-$  and  $-CH_2CH(CH_3)-$ ; p is 0-50; a is 0-2; z is 1-3.

Introducing oxyalkylene units in the organopolysiloxane will increase the hydrophilicity of the binder, especially when ethyleneoxide type  $-[CH_2CH_2-O]-$  is used.

In a further embodiment, the hydrophilic modification of the binder consists of both A-B-A 20 modifications (as described above) and of pendant hydrophilic oligomer/polymer moieties.

Preferred cross-linkers are those selected from tetramethoxysilane, tetraethoxysilane; tetrapropoxysilane; tetra-*n*-butoxysilane; vinyltris(methylethoxyimino)silane; vinyltris-(acetoxime)silane; methyltris(methylethoxyimino)silane; methyltris(acetoxime)silane; vinyltrimethoxysilane; methyltrimethoxysilane; vinyltris(isopropenoxy)silane; 25 tetraacetoxysilane; methyltriacetoxysilane; ethyltriacetoxysilane; vinyltriacetoxysilane; di-*t*-butoxydiacetoxysilane; methyltris(ethylactate)silane and vinyltris(ethylactate)silane as well as hydrolysis-condensation products of the same.

Other interesting cross-linkers are those selected from vinyltriethoxysilane, methyltriethoxysilane, ethyltrimethoxysilane, ethyltrimethoxysilane, tetraisopropoxysilane, tetrabutoxysilane as well as hydrolysis-condensation products of the same.

In some interesting embodiments, the polysiloxane-based binder comprises a

5 polydimethylsiloxane-based binder.

In other interesting embodiments, the binder may include fluoro-modifications, e.g. fluoroalkyl modified polysiloxane binders such as silanol-terminated poly(trifluoropropyl-methylsiloxane).

The polysiloxane-based binder system typically constitutes at least 40 % by dry weight, such

10 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.

#### *Coating compositions*

In view of the above, the cured coating may be prepared from a range of different

15 combinations of reactive polysiloxanes and silanes.

Hence, in one embodiment, the invention provides a fouling control coating composition comprising a polysiloxane-based binder system, said binder system comprising one or more polysiloxane components modified with hydrophilic oligomer/polymer moieties, and one or more biocides, wherein the weight ratio between the hydrophilic oligomer/polymer moieties

20 and the one or more biocides is in the range 1:0.02 to 1:20, in particular 1:0.05 to 1:10, and wherein more than 50 % by weight of the binder system is represented by polysiloxane parts.

In another embodiment, the invention provides a fouling control coating composition comprising a polysiloxane-based binder system, said binder system comprising one or more

25 hydrophilic oligomer/polymer moieties which at one or both ends carry  $-\text{Si}(\text{R}^*)_3$  groups, wherein each  $\text{R}^*$  independently is selected from  $\text{C}_{1-4}$ -alkyl and  $\text{C}_{1-4}$ -alkoxy (e.g. methyl, ethyl, propyl, butyl, methoxy, ethoxy, propoxy, and butoxy), at least one being  $\text{C}_{1-4}$ -alkoxy, or  $\text{R}^*$  is another condensation curable termination, at least one being  $\text{C}_{1-4}$ -alkoxy, or at least one being another curable termination, and one or more biocides, wherein the weight ratio

30 between the hydrophilic oligomer/polymer moieties and the one or more biocides is in the

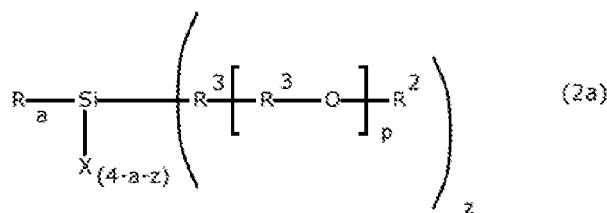
range 1:0.02 to 1:20, and wherein more than 50 % by weight of the binder system is represented by polysiloxane parts.

In one embodiment, the one or more hydrophilic oligomer/polymer moieties carry at only one end  $-\text{Si}(\text{R}^*)_3$  groups. In this way, it is possible to construct a binder of a polysiloxane chain 5 having grafts of the hydrophilic oligomer/polymer moieties.

In another embodiment, the one or more hydrophilic oligomer/polymer moieties carry at both ends  $-\text{Si}(\text{R}^*)_3$  groups. During curing, the hydrophilic component will be incorporated in the crosslinked network and constitute a non-hydrolysable hydrophilic moiety. In this way, it is possible to construct a binder of a polysiloxane chain interrupted by segments of the 10 hydrophilic oligomer/polymer moieties, which are connected through the crosslinking sites.

In a still further embodiment, the invention provides a fouling control coating composition comprising a polysiloxane-based binder system, said binder system comprising a cross-linker of formula (2) above, wherein R represents a poly(oxyalkylene), and one or more biocides, wherein the weight ratio between the poly(oxyalkylene)) and the one or more biocides is in 15 the range 1:0.02 to 1:20.

In a still further embodiment, the invention provides a fouling control coating composition comprising a polysiloxane-based binder system, said binder system comprising a cross-linker of formula (2a)



20 wherein, each R represents, independently, an unsubstituted or substituted monovalent hydrocarbon group of 1 to 6 carbon atoms or a hydrolysable group; each X represents, independently, a hydrolysable group; each R<sup>2</sup> is independently selected from -H, C<sub>1-4</sub>-alkyl (e.g. -CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, -CH(CH<sub>3</sub>)<sub>2</sub>, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), phenyl (-C<sub>6</sub>H<sub>5</sub>), and C<sub>1-4</sub>-alkylcarbonyl (e.g. -C(=O)CH<sub>3</sub>, -C(=O)CH<sub>2</sub>CH<sub>3</sub> and -C(=O)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), in particular -H and methyl; each R<sup>3</sup> is independently selected from C<sub>2-5</sub>-alkylene (e.g. -CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CH(CH<sub>3</sub>)-, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CH(CH<sub>2</sub>CH<sub>3</sub>)-), arylene (e.g. 1,4-phenylene) and C<sub>2-5</sub>-

25

alkylene substituted with aryl (e.g. 1-phenyl ethylene), in particular from C<sub>2-5</sub>-alkylene such as -CH<sub>2</sub>CH<sub>2</sub>- and -CH<sub>2</sub>CH(CH<sub>3</sub>)-); p is 0-50; a is 0-2; z is 1-3;

and one or more biocides, wherein the weight ratio between the poly(oxyalkylene) and the one or more biocides is in the range 1:0.02 to 1:20, and wherein more than 50 % by weight

5 of the binder system is represented by polysiloxane parts.

In one variant of the above embodiments, the hydrophilic oligomer/polymer moieties are selected from poly(vinyl pyrrolidone), poly[N-(2-hydroxypropyl)methacrylamide], poly(acrylic acid), poly(glycerol), polyHEMA, polysaccharides, poly(vinyl alcohol), polyketones, poly(aldehyde guluronate), polyvinylamine, polycaprolactones, poly(vinyl acetate),

10 polyoxyalkylenes like poly(ethylene glycol), poly(propylene glycol), poly(2-methyl-2-oxazoline), including copolymers of the foregoing, in particular poly(oxyalkylenes), especially from polyoxyethylene, polyoxypropylene and poly(oxyethylene-co-oxypropylene).

The term "polysiloxane-based binder system" is intended to mean that the binder system mainly consists of polysiloxane parts, i.e. that more than 50 % by weight, preferably more

15 than 60 % by weight, e.g. more than 70 % by weight, of the binder system is represented by polysiloxane parts. Preferably, the polysiloxane parts constitute 50-99.99 % by weight, e.g. 50-99.9 % by weight, in particular 60-99.5 % by weight, or 50-99 % by weight, or 60-98 % by weight, or 70-97 % by weight, or even 70-99 % by weight, or 80-98 % by weight, or 90-97 % by weight, of the binder system (i.e. the binder components and any cross-linkers).

20 The remainder of the binder system is preferably made of the hydrophilic oligomer/polymer moieties and any (non-polysiloxane-type) cross-linkers. This being said, the hydrophilic oligomer/polymer moieties preferably makes up 1-30 % by weight, such as 2-20 % by weight, e.g. 1-10 % by weight, of the binder system.

### *Biocides*

25 The coating composition used for forming a cured fouling control coat also includes 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.

30 Illustrative examples of biocides are those selected from metallo-dithiocarbamates such as bis(dimethylthiocarbamato)zinc, ethylene-bis(dithiocarbamato)zinc, ethylene-bis(dithio-

carbamato)manganese, and complexes between these; bis(1-hydroxy-2(1H)-pyridine-thionato-O,S)-copper; copper acrylate; bis(1-hydroxy-2(1H)-pyridinethionato-O,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 5 thiocyanate, basic copper carbonate, copper hydroxide, barium metaborate, and copper sulphide; heterocyclic nitrogen compounds such as 3a,4,7,7a-tetrahydro-2-((trichloromethyl)-thio)-1H-isoindole-1,3(2H)-dione, pyridine-triphenylborane, 1-(2,4,6-trichlorophenyl)-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 10 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<sup>®</sup>-211N), 1,2-benzisothiazolin-3-one, and 2-(thiocyanatomethylthio)-benzothiazole; urea derivatives such as N-(1,3-bis(hydroxymethyl)-2,5-dioxo-4-imidazolidinyl)-N,N'-bis(hydroxymethyl)urea, and N-(3,4-dichlorophenyl)-N,N-dimethylurea, N,N-dimethylchlorophenylurea; amides or imides of 15 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-nitriolo-propionamide, 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- 20 didecyl-N-methyl-poly(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-((dimethylamino)-sulfonyl)-1-fluoro-N-phenylmethanesulfenamide, and 1-((diiodomethyl)sulfonyl)-4- 25 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 compound, such as medetomidine; 2-(p-chlorophenyl)-3-cyano-4-bromo-5-trifluoromethyl pyrrole and mixtures thereof.

30 Presently, it is preferred that the biocide does not comprise tin.

Currently preferred biocides are those selected from the group consisting of 2,4,5,6-tetrachloroisopthalonitrile (Chlorothalonil), copper thiocyanate (cuprous sulfocyanate), N-dichloro-fluoromethylthio-N',N'-dimethyl-N-phenylsulfamide (Dichlofluanid), 3-(3,4-dichlorophenyl)-1,1-dimethylurea (Diuron), N<sup>2</sup>-tert-butyl-N<sup>4</sup>-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), N<sup>2</sup>-tert-butyl-N<sup>4</sup>-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(1-5 hydroxy-2(1H)-pyridinethionato-O,S)-(T-4) zinc (zinc pyridinethione; zinc pyrithione), bis(1-hydroxy-2(1H)-pyridinethionato-O,S)-T-4) copper (copper pyridinethione; copper pyrithione; Copper Omadine), zinc ethylene-1,2-bis-dithiocarbamate (zinc-ethylene-N-N'-dithiocarbamate; Zineb), copper(i) oxide, metallic copper, 3-(3,4-dichlorophenyl)-1,1-dimethylurea (Diuron) and diiodomethyl-p-tolylsulfone; Amical 48. Preferably at least one 10 biocide is selected from the above list.

In a particularly preferred embodiment, the biocides are preferably selected among biocides which are effective against soft fouling such as slime and algae. Examples of such biocides are N<sup>2</sup>-tert-butyl-N<sup>4</sup>-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)-15 pyridinethionato-O,S)-(T-4) zinc (zinc pyridinethione; zinc pyrithione), bis(1-hydroxy-2(1H)-pyridinethionato-O,S)-T-4) copper (copper pyridinethione; copper pyrithione) 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-O,S)-T-4) copper (copper pyridinethione; copper pyrithione; Copper 20 Omadine).

In a further particularly preferred embodiment, 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 25 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. 30 mechanical integrity, drying times, etc.).

In a particularly preferred embodiment, the biocide is encapsulated 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (Sea-Nine CR2).

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.

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.

The relative weight ratio between the hydrophilic oligomer/polymer moieties and the one or more biocides is typically in the range of 1:0.02 to 1:20, or 1:0.05 to 1:20, or 1:0.06 to

5 1:16, or 1:0.08 to 1:12, or 1:0.05 to 1:10, or 1:0.1 to 1:10, even 1:0.15 to 1:6, or 1:0.05 to 1:5, or 1:0.1 to 1:5, or 1:0.2 to 1:4. In other embodiments, the relative weight ratio between the hydrophilic oligomer/polymer moieties and the one or more biocides is typically in the range of 1:0.02 to 1:20, or 1:0.05 to 1:20, or 1:0.06 to 1:16, or 1:0.08 to 1:14, or 1:0.1 to 1:12, or 1:0.05 to 1:10, even 1:0.15 to 1:10, or 1:0.05 to 1:9, or 1:0.1 to 1:8, or

10 1:0.2 to 1:7.

### *Catalyst*

The coating composition used for forming a cured fouling control coat may further comprise a condensation catalyst to accelerate the cross-linking. Examples of suitable catalysts include organometal- and metal salts of organic carboxylic acids, such as dibutyl tin dilaurate, dibutyl

15 tin diacetate, dibutyl tin dioctoate, dibutyl tin 2-ethylhexanoate, dioctyl tin dilaurate, dioctyl tin diacetate, dioctyl tin dioctoate, dioctyl tin 2-ethylhexanoate, dioctyltin di neodecanoate, tin naphthenate, tin butyrate, tin oleate, tin caprylate, bismuth 2-ethylhexanoate, bismuth octanoate, bismuth neodecanoate, iron 2-ethylhexanoate, lead 2-ethylloctoate, cobalt-2-ethylhexanoate, manganese 2-ethylhexanoate, zinc 2-ethylhexanoate, zinc naphthenate, zinc 20 stearate, cobalt naphthenate and titanium naphtenate; titanate- and zirconate esters such as tetrabutyl titanate, tetrakis(2-ethylhexyl)titanate, triethanolamine titanate, tetra(isopropenyloxy)-titanate, titanium tetrabutanolate, titanium tetrabutylpropanolate; titanium tetraisopropanolate, zirconium tetrapropanolate, zirconium tetrabutanolate; chelated titanates such as diisopropyl bis(acetylacetonyl)titanate. Further catalysts include tertiary 25 amines, such as triethylamine, tetramethylmethylenediamine, pentamethyldiethylenetriamine and 1,4-ethylenepiperazine. Further examples include guanidine based catalysts. Even further examples of condensation catalysts are described in WO 2008/132196 and US 2004/006190.

The catalyst may be used alone or as combination of two or more catalysts. The amount of 30 catalyst to be used is depending on the reactivity of the catalyst and the cross-linker(s) and desired drying time. In a preferred embodiment the catalyst concentration is between 0.01-10 %, e.g. 0.01-3.0 %, or 5.0-10 %, or 0.1-4.0 %, or 1.0-6.0 %, by weight of the total combined amount of the binder (i) and cross-linking agent (ii).

In some embodiments, a catalyst is not included.

*Hydrophilic-modified polysiloxane oils*

The composition may further include hydrophilic-modified polysiloxane oils, i.e. constituents which do not form covalent bonds to the polysiloxane-based binder matrix. Hydrophilic-

5 modified polysiloxane oils are widely used as surfactants and emulsifiers due to the content of both hydrophilic and lipophilic groups in the same molecule. In contrast to the polysiloxane components discussed above, the hydrophilic-modified polysiloxane oils are selected so that they do not contain groups that can react with the binder (or binder components) or the cross-linker (if present), hence the hydrophilic-modified polysiloxane oils are intended to be  
10 non-reactive, in particular with respect to the binder components. In particular, the hydrophilic-modified polysiloxane oils are devoid of any silicon-reactive groups such as Si-OH groups, hydrolysable groups such as Si-OR (such as alkoxy, oxime, acetoxy etc.) groups, etc., so as to avoid reaction with constituents of the polysiloxane-based binder system.

The non-reactive hydrophilic-modified polysiloxane oils are typically modified by the addition

15 of non-ionic oligomeric or polymeric groups which can be polar and/or capable of hydrogen bonding, enhancing their interaction with polar solvents, in particular with water, or with other polar oligomeric or polymeric groups. Examples of these groups include, amides (e.g. poly(vinyl pyrrolidone), poly[N-(2-hydroxypropyl)methacrylamide]), poly(N,N-dimethacrylamide), acids (e.g. poly(acrylic acid)), alcohols (e.g. poly(glycerol), polyHEMA, 20 polysaccharides, poly(vinyl alcohol)), ketones (polyketones), aldehydes (e.g. poly(aldehyde guluronate), amines (e.g. polyvinylamine), esters (e.g. polycaprolactones, poly(vinyl acetate)), ethers (e.g. polyoxyalkylenes like poly(ethylene glycol), poly(propylene glycol)), imides (e.g. poly(2-methyl-2-oxazoline)), etc., including copolymers of the foregoing. Preferably the hydrophilicity is obtained by modification with polyoxyalkylene groups.

25 As before, it should be understood that the hydrophilic oligomer/polymer moieties with which the polysiloxane oils are modified are of non-silicon origin. Preferably, the above-mentioned "oligomers" and "polymers" include at least 3 repeating units, such as at least 5 repeating units. In many interesting embodiments, the oligomers or polymers include 3-1,000 repeating units, such as 3-200, or 5-150, or 5-100 repeating units.

30 In some preferred embodiments, the hydrophilic groups (i.e. oligomeric or polymeric groups) have a number average molecular weight ( $M_n$ ) in the range of 100-50,000 g/mol, such as in the range of 100-30,000 g/mol, in particular in the range of 200-20,000 g/mol, or in the range of 200-10,000 g/mol.

In the present description with claims, the term "hydrophilic-modified" in the context of "hydrophilic-modified polysiloxane oil" is intended to mean that the oligomeric or polymeric groups with which the polysiloxane is modified, in themselves (i.e. as discrete molecules) have a solubility of at least 1 % (w/w) in demineralized water at 25°C.

5 Of particular interest are those hydrophilic-modified polysiloxane oils in which the relative weight of the hydrophilic moieties is 1% or more of the total weight (e.g. 1-90%), such as 5% or more (e.g. 5-80%), in particular 10% or more (e.g. 10-70%) of the total weight of the hydrophilic-modified polysiloxane oil.

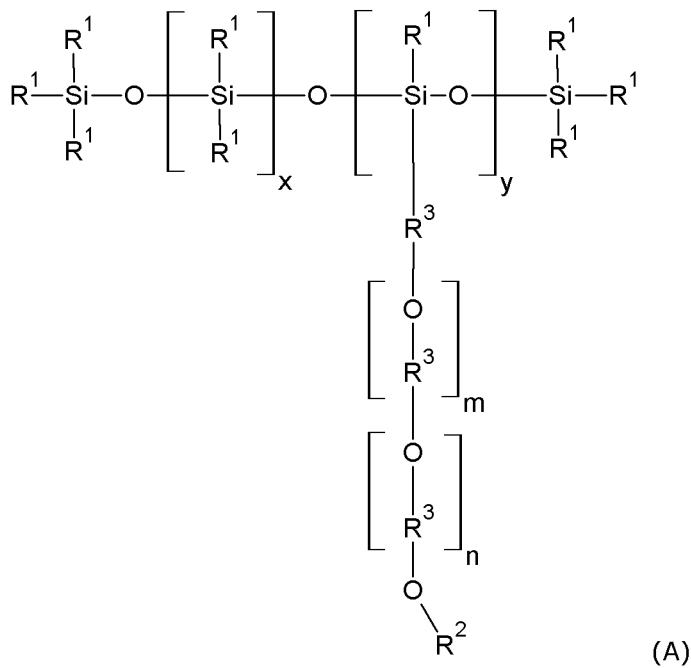
10 In a preferred embodiment, the hydrophilic-modified polysiloxane oil (if present) has a number average molecular weight ( $M_n$ ) in the range of 100-100,000 g/mol, such as in the range of 250-75,000 g/mol, in particular in the range of 500-50,000 g/mol.

It is also preferred if the hydrophilic-modified polysiloxane oils (if present) have a viscosity in the range of 10-20,000 mPa·s, such as in the range of 20-10,000 mPa·s, in particular in the range of 40-5,000 mPa·s.

15 In addition to the utilization of the polysiloxane components modified with hydrophilic oligomer/polymer moieties, the hydrophilic-modified polysiloxane oils may be utilized to control the leaching of the biocide.

In one currently preferred embodiment, the hydrophilic-modified polysiloxane oil is a poly(oxyalkylene)-modified polysiloxane.

20 In one variant hereof, the poly(oxyalkylene)-modified polysiloxane oil is a polysiloxane having grafted thereto poly(oxyalkylene) chains. An illustrative example of the structure of such hydrophilic-modified polysiloxane oils is formula (A):



wherein each  $R^1$  is independently selected from  $C_{1-5}$ -alkyl (including linear or branched hydrocarbon groups) and aryl (e.g. phenyl ( $-C_6H_5$ )), in particular methyl;

each  $R^2$  is independently selected from -H,  $C_{1-4}$ -alkyl (e.g.  $-CH_3$ ,  $-CH_2CH_3$ ,

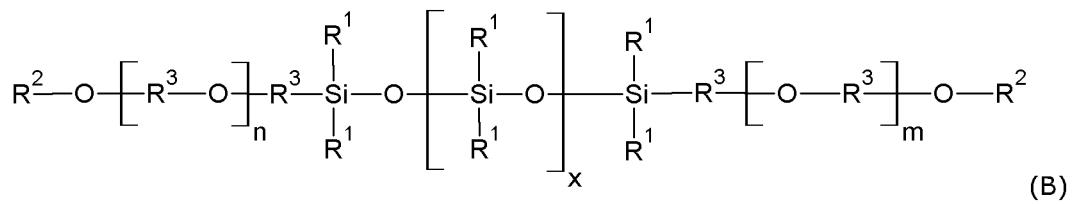
5  $-CH_2CH_2CH_3$ ,  $-CH(CH_3)_2$ ,  $-CH_2CH_2CH_2CH_3$ , phenyl ( $-C_6H_5$ ), and  $C_{1-4}$ -alkylcarbonyl (e.g.  $-C(=O)CH_3$ ,  $-C(=O)CH_2CH_3$  and  $-C(=O)CH_2CH_2CH_3$ ), in particular -H and methyl; each  $R^3$  is independently selected from  $C_{2-5}$ -alkylene (e.g.  $-CH_2CH_2-$ ,  $-CH_2CH(CH_3)-$ ,  $-CH_2CH_2CH_2-$ ,  $-CH_2CH_2CH_2CH_2-$ ,  $-CH_2CH(CH_2CH_3)-$ ), arylene (e.g. 1,4-phenylene) and  $C_{2-5}$ -alkylene substituted with aryl (e.g. 1-phenyl ethylene), in particular from  $C_{2-5}$ -alkylene such as

10  $-CH_2CH_2-$  and  $-CH_2CH(CH_3)-$ );  $x$  is 0-2500,  $y$  is 1-100 and  $x+y$  is 1-2000; and  $n$  is 0-50,  $m$  is 0-50 and  $m+n$  is 1-50.

Commercially available hydrophilic-modified polysiloxane oils of this type are DC5103 (Dow Corning), DC Q2-5097 (Dow Corning), and DC193 (Dow Corning).

In another variant hereof, the poly(oxyalkylene)-modified polysiloxane oil is a polysiloxane

15 having incorporated in the backbone thereof poly(oxyalkylene) chains. An illustrative example of the structure of such hydrophilic-modified polysiloxane oils is formula (B):



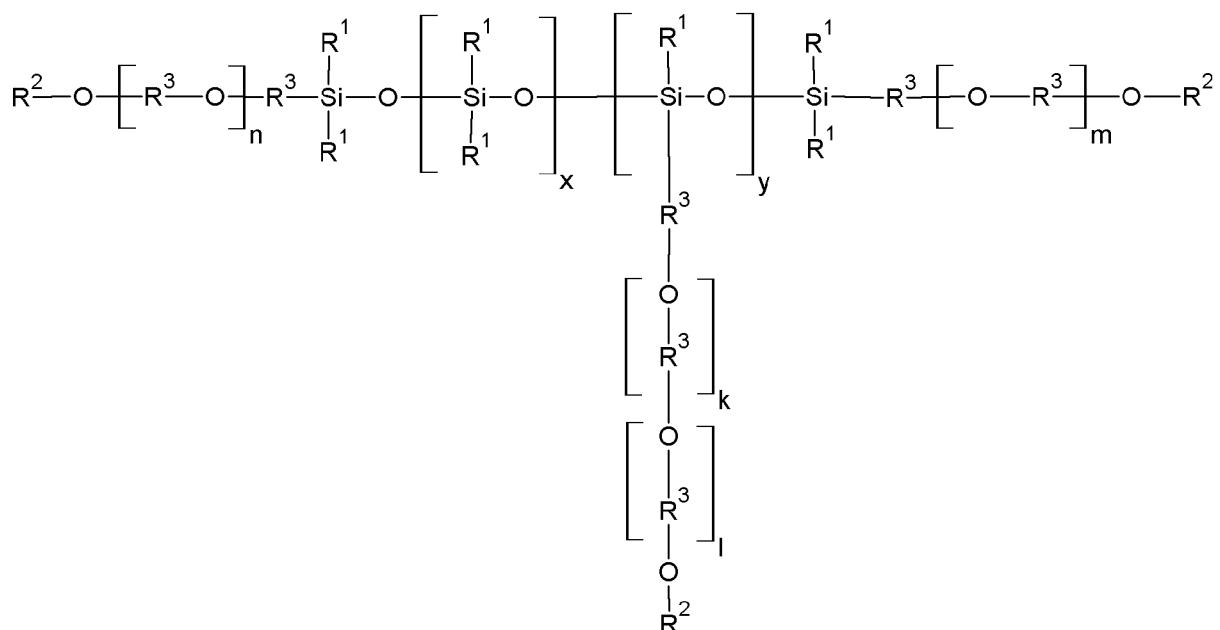
wherein each  $\text{R}^1$  is independently selected from  $\text{C}_{1-5}$ -alkyl (including linear or branched hydrocarbon groups) and aryl (e.g. phenyl ( $-\text{C}_6\text{H}_5$ )), in particular methyl; each  $\text{R}^2$  is independently selected from -H,  $\text{C}_{1-4}$ -alkyl (e.g.  $-\text{CH}_3$ ,  $-\text{CH}_2\text{CH}_3$ ,  $-\text{CH}_2\text{CH}_2\text{CH}_3$ ,

5  $-\text{CH}(\text{CH}_3)_2$ ,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ , phenyl ( $-\text{C}_6\text{H}_5$ ), and  $\text{C}_{1-4}$ -alkylcarbonyl (e.g.  $-\text{C}(=\text{O})\text{CH}_3$ ,  $-\text{C}(=\text{O})\text{CH}_2\text{CH}_3$  and  $-\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{CH}_3$ ), in particular -H and methyl; each  $\text{R}^3$  is independently selected from  $\text{C}_{2-5}$ -alkylene (e.g.  $-\text{CH}_2\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}(\text{CH}_3)-$ ,  $-\text{CH}_2\text{CH}_2\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)-$ ), arylene (e.g. 1,4-phenylene) and  $\text{C}_{2-5}$ -alkylene substituted with aryl (e.g. 1-phenyl ethylene), in particular from  $\text{C}_{2-5}$ -alkylene such as

10  $-\text{CH}_2\text{CH}_2-$  and  $-\text{CH}_2\text{CH}(\text{CH}_3)-$ ;  $x$  is 0-2500; and  $n$  is 0-50,  $m$  is 0-50 and  $m+n$  is 1-50.

Commercially available hydrophilic-modified polysiloxane oils of this type are DC Q4-3669 (Dow Corning), DC Q4-3667 (Dow Corning) and DC2-8692.

In still another variant hereof, the poly(oxyalkylene)-modified polysiloxane oil is a polysiloxane having incorporated in the backbone thereof polyoxyalkylene chains and having grafted thereto polyoxyalkylene chains. An illustrative example of the structure of such 15 hydrophilic-modified polysiloxane oils is formula (C):



wherein each R<sup>1</sup> is independently selected from C<sub>1-5</sub>-alkyl (including linear or branched hydrocarbon groups) and aryl (e.g. phenyl (-C<sub>6</sub>H<sub>5</sub>)), in particular methyl; each R<sup>2</sup> is independently selected from -H, C<sub>1-4</sub>-alkyl (e.g. -CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, -CH(CH<sub>3</sub>)<sub>2</sub>, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), phenyl (-C<sub>6</sub>H<sub>5</sub>), and C<sub>1-4</sub>-alkylcarbonyl (e.g. -C(=O)CH<sub>3</sub>, -C(=O)CH<sub>2</sub>CH<sub>3</sub> and -C(=O)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), in particular -H and methyl; each R<sup>3</sup> is independently selected from C<sub>2-5</sub>-alkylene (e.g. -CH<sub>2</sub>CH<sub>2</sub>-), -CH<sub>2</sub>CH(CH<sub>3</sub>)-, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CH(CH<sub>2</sub>CH<sub>3</sub>)-), arylene (e.g. 1,4-phenylene) and C<sub>2-5</sub>- alkylene substituted with aryl (e.g. 1-phenyl ethylene), in particular from C<sub>2-5</sub>-alkylene such as -CH<sub>2</sub>CH<sub>2</sub>- and -CH<sub>2</sub>CH(CH<sub>3</sub>)-); x is 0-2500, y is 1-100 and x+y is 1-2000; k is 0-50, l is 0-50 and k+l is 1-50; and n is 0-50, m is 0-50 and m+n is 1-50.

In the above structures (A), (B) and (C), the groups -CH<sub>2</sub>CH(CH<sub>3</sub>)-, -CH<sub>2</sub>CH(CH<sub>2</sub>CH<sub>3</sub>)-, etc. may be present in any of the two possible orientations. Similarly, it should be understood that the segments present x and y times typically are randomly distributed, or distributed as blocks, within the polysiloxane structure.

In these embodiments and variants, the poly(oxyalkylene) is preferably selected from polyoxyethylene, polyoxypropylene and poly(oxyethylene-co-oxypropylene), which sometimes are referred to as poly(ethylene glycol), poly(propylene glycol) and poly(ethylene glycol-co-propylene glycol). Hence, in the above structures (A), (B) and (C), each R<sup>3</sup> linking two oxygen atoms is preferably selected from -CH<sub>2</sub>CH<sub>2</sub>- and -CH<sub>2</sub>CH(CH<sub>3</sub>)-, whereas each R<sup>3</sup> linking a silicon atom and an oxygen atom preferably is selected from C<sub>2-5</sub>-alkyl.

It should be understood that the one or more non-reactive hydrophilic-modified polysiloxane oils if present may be of different types, e.g. two or more of the types described above.

The one or more hydrophilic-modified polysiloxane oils are included in the coating composition in an amount of 0.01-20 %, e.g. 0.05-10 %, by dry weight. In certain embodiments, the one or more hydrophilic-modified polysiloxane oils constitutes 0.05-7 % by dry weight, e.g. 0.1-5 % by dry weight, in particular 0.5-3 % by dry weight, of the coating composition. In certain other embodiments, the one or more hydrophilic-modified polysiloxane oils constitutes 1-10 % by dry weight, e.g. 2-9 % by dry weight, in particular 2-7 % by dry weight, or 3-7 % by dry weight, or 3-5 % by dry weight, or 4-8 % by dry weight, of the coating composition.

When the one or more hydrophilic-modified polysiloxane oil are included, the ratio between on the one hand the combined amount of the hydrophilic oligomer/polymer moieties of the binder matrix and the one or more hydrophilic-modified polysiloxane oil(s) and on the other hand the one or more biocides is typically in the range of 1:0.02 to 1:20, or 1:0.05 to 1:20,

or 1:0.06 to 1:16, or 1:0.08 to 1:12, or 1:0.1 to 10, even 1:0.15 to 1:6, or 1:0.1 to 1:5, or 1:0.2 to 1:4. In other embodiments, the ratio between on the one hand the combined amount of the hydrophilic oligomer/polymer moieties of the binder matrix and the one or more hydrophilic-modified polysiloxane oil(s) and on the other hand the one or more biocides 5 is typically in the range of 1:0.02 to 1:20, or 1:0.05 to 1:20, or 1:0.06 to 1:16, or 1:0.08 to 1:14, or 1:0.1 to 12, even 1:0.15 to 1:10, or 1:0.05 to 1:9, or 1:0.1 to 1:8, or 1:0.2 to 1:7.

In should be understood, that in some embodiments, the paint coat (and the coating composition) is completely devoid of any hydrophilic-modified polysiloxane oils. In some other embodiment, the paint composition (and the coating composition) is also devoid of any 10 of the non-reactive fluids mentioned under "additives" (i) and any fluorinated oils (cf. immediately below). Such compositions may be referred to as "oil free".

#### *Fluorinated oils*

As an alternative to, or in addition to, the hydrophilic-modified polysiloxane oils, the coating composition (and thereby the paint coat) may have included therein one or more fluorinated 15 oil(s). By the term "oil" is inherently meant that the constituent does not form covalent bonds to the polysiloxane-based binder matrix. Hence, the fluorinated oil(s) do not contain groups that can react with the binder (or binder components) or the cross-linker (if present), hence the one or more fluorinated oil(s) are intended to be non-reactive, in particular with respect to the binder components. In particular, the fluorinated oils are devoid of any silicon-reactive 20 groups such as Si-OH groups, hydrolysable groups such as Si-OR (such as alkoxy, oxime, acetoxy etc.) groups, etc., so as to avoid reaction with constituents of the polysiloxane-based binder system.

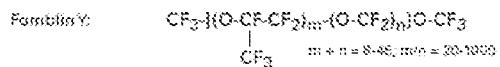
It is preferred that the one or more fluorinated oil(s) (if present) have a viscosity in the range 25 of 10-20,000 mPa·s, such as in the range of 20-10,000 mPa·s, in particular in the range of 40-5,000 mPa·s.

In a preferred embodiment, the fluorinated oil(s) (if present) has a number average molecular weight ( $M_n$ ) in the range of 100-100,000 g/mol, such as in the range of 250-75,000 g/mol, in particular in the range of 500-50,000 g/mol.

The one or more fluorinated oils may be utilized to control the accessibility of the one or 30 more enzymes and/or to control the leaching of any biocides, as well as to distribute the enzyme in the wet paint.

In one embodiment, the one or more fluorinated oils are selected from fluoroalkyl modified oils, e.g. perfluorinated oils, perfluoroalkyl-modified polysiloxane, perfluoro siloxane, perfluoro polyether, perfluorinated alkanes, or perfluoroalkyl modified polyalkylene oxide, perfluoro polyalkylene oxide.

5 Commercially available examples of such oils are:



Lumiflon LF-200: (Fluoroethylene-Alkyl Vinyl Ether) alternating copolymer.

In another embodiment, the one or more fluorinated oils are selected from fluoroalkyl modified polyoxyalkylene polysiloxane oils (e.g. PEG-PDMS). These compounds are

10 polysiloxanes which have been modified with a fluoroalkyl group and polyoxyalkylene, and can have a linear or branched/pendant conformation, or a combination of a linear and branched/pendant conformation. In the linear form, the polymer will generally have the structure A-B-C where A is a fluoroalkyl group, B is a polysiloxane and C is a polyoxyalkylene. Therefore, it will only have one fluoroalkyl group and one polyoxyalkylene group per

15 polysiloxane molecule. In a variation, the modification of the polysiloxane molecule is in a branched/pendant conformation, in which the fluoroalkyl group(s) and the polyoxyalkylene group(s) are attached to the polysiloxane backbone in non-terminal positions. This allows more than one of each group per polysiloxane molecule. Examples of possible synthetic routes are disclosed in US 5,445,114.

20 This type of fluorinated oils appears to provide certain advantages. Without being bound to any particular theory, it is believed (i) that the migration of the oils to the surface of the coating during curing may be higher due to the fluorination; (ii) that the fluorination may lower the affinity of the oil to adsorb to pigments compared to non-fluorinated analogues.

25 Commercially available examples of such oils are Fluorosil 2110, a perfluoro nonyl ethyl PEG-8 dimethicone and C1910, a fluorinated silicone polyether of the same generic structure as Fluorosil 2110.

It should be understood that the one or more non-reactive fluorinated oil(s), if present, may be of different types, e.g. two or more of the types described above.

If present, the one or more fluorinated oils are typically included in the coating composition in an amount of 0.01-20 %, e.g. 0.05-10 %, by dry weight. In certain embodiments, the one or more fluorinated oils constitutes 0.05-7 % by dry weight, e.g. 0.1-5 % by dry weight, in particular 0.5-3 % by dry weight, of the coating composition. In certain other embodiments,

5 the one or more fluorinated oils constitutes 1-10 % by dry weight, e.g. 2-9 % by dry weight, in particular 2-7 % by dry weight, or 3-7 % by dry weight, or 3-5 % by dry weight, or 4-8 % by dry weight, of the coating composition.

Also, if present together with one or more hydrophilic-modified polysiloxane oils, the one or more fluorinated oils and the one or more hydrophilic-modified polysiloxane oils are typically

10 included in the coating composition in a combined amount of 0.01-20 %, e.g. 0.05-10 %, by dry weight. In certain embodiments, the one or more fluorinated oils constitutes 0.05-7 % by dry weight, e.g. 0.1-5 % by dry weight, in particular 0.5-5 % by dry weight, of the coating composition. In certain other embodiments, the one or more fluorinated oils constitutes 1-10 % by dry weight, e.g. 2-9 % by dry weight, in particular 2-7 % by dry weight, or 3-7 % by dry weight, or 2-6 % by dry weight, or 3-5 % by dry weight, or 4-8 % by dry weight, of the coating composition.

#### *Solvents, additives, pigments and fillers*

The coating composition used for forming a cured fouling control coat may further comprise solvents and additives.

20 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; octamethyltrisiloxane, and mixtures thereof. Alternatively, the solvent system may include water or be water-based (>50% water in the solvent system).

25 In one embodiment, the solvents are selected from 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; octamethyltrisiloxane, and mixtures thereof, preferably those solvents having a boiling point of 110 °C or more.

30 The solvents, if any, typically constitute 5-50 % by volume of the coating composition.

Examples of additives are:

- (i) non-reactive fluids such as 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-5 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 821-10 823 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,

20 etc.

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. 25 0.6-4 %, by dry weight of the coating composition.

Furthermore, the coating composition used for forming a cured fouling control coat may comprise pigments and fillers.

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 30 properties. "Pigments" are normally characterised in that they render the final paint coating non-transparent and non-translucent, whereas "fillers" normally are characterised in that they do not render the paint 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, 5 chromium oxide, isoindoline orange, bis-acetoacet-o-tolidiole, benzimidazolon, quinaphtalone yellow, isoindoline yellow, tetrachloroisoindolinone, quinophthalone yellow.

Examples of fillers are calcium carbonate such as calcite, dolomite, talc, mica, feldspar, barium sulfate, kaolin, nephelin, silica, perlite, magnesium oxide, and quartz flour, etc. Fillers (and pigments) may also be added in the form of nanotubes or fibres, thus, apart from the 10 before-mentioned examples of fillers, the coating composition may also comprise fibres, 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 15 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

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 20 200-4,000 mPa·s.

#### *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 25 etc. The coating compositions are typically prepared and shipped as two- or three-component systems that should be combined and thoroughly mixed immediately prior to use. The paints 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 30 suitable preparation method is described in the Examples.

The coating composition to be used in the method of the invention is typically prepared by mixing two or more components e.g. two pre-mixtures, one pre-mixture comprising the one

or more reactive polysiloxane binders and one pre-mixture comprising the one or more cross-linking agents. It should be understood that when reference is made to the coating composition, it is the mixed coating composition ready to be applied. Furthermore, all amounts stated as % by dry weight of the coating composition should be understood as % by 5 dry weight of the mixed paint composition ready to be applied, i.e. the weight apart from the solvents (if any).

*Specific embodiments of the paint coat*

In one preferred embodiment the paint coat (preferably a top coat) comprises:

(i) 60-98 % by dry weight, or 70-93 % by dry weight, of the total paint coat composition of

10 one or more reactive polydiorganosiloxanes (e.g. silanol-terminated polysiloxanes), one or more reactive polysiloxanes modified with hydrophilic oligomer/polymer moieties selected from poly(oxyalkylene)s and a cross-linker; and

(ii) 0.1-15 % by dry weight, or 0.5-8 % by dry weight, of the total paint coat composition of one or more organic biocides,

15 wherein the weight ratio between the hydrophilic oligomer/polymer moieties and the one or more biocides is in the range 1:0.1 to 1:10.

In another preferred embodiment, the binder in the preferred embodiment above mentioned, has been pre-reacted in a moisture free environment to form a single component formulation by admixing 100 parts by weight of silanol terminated polydiorganosiloxane with 0.5-30 parts 20 by weight of hydrolysable cross-linker, such as vinyltrimethoxysilane or a vinyloximosilane.

In the above embodiments, the remainder of the paint coat (up to 100 % by dry weight) is preferably made up of one or more constituents selected from additives, catalysts, pigments, fillers, and hydrophilic-modified polysiloxane oils (preferably those selected from the poly(oxyalkylene)-modified polysiloxane oils).

25 Preferably, the paint coats according to the above embodiments include additives, pigments and fillers in the amounts specified further above.

*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.

The term "applying" is used in its normal meaning within the paint industry. Thus, "applying"

5 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 applied in a dry film thickness of 50-600 µm, such as 50-500 µm, e.g. 75-  
10 400 µm, or 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 up to at least 200 µm, preferably up to at least 400 µm, and in particular up  
15 to at least 600 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, aluminium, or glass-fibre reinforced polyester. In the most interesting embodiments, the substrate is a metal substrate, in particular a steel substrate. In an alternative embodiment, the substrate is a glass-fibre reinforced polyester substrate. In some embodiments, the substrate is at least a  
25 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 (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  
30 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 other aquatic culture installations, and buoys, etc.

The surface of the substrate may either be the "native" surface (e.g. the steel surface). However, the substrate is typically coated, e.g. with 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 5  $\mu\text{m}$ , such as 150-450  $\mu\text{m}$ , e.g. 200-400  $\mu\text{m}$ . Alternatively, the substrate may carry a paint coat, e.g. a worn-out fouling control paint coat, or similar.

In one important embodiment, the substrate is a metal substrate (e.g. a steel substrate) coated with an anticorrosive coating such as an anticorrosive epoxy-based coating, e.g. cured 10 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 15 epoxy primer coating.

It should be understood that the expression "fouling release" (as well as "fouling control") relates to all types of bio-fouling of a surface (i.e. settlement of organisms on a surface), in particular surfaces exposed to an aqueous environment or to aqueous liquids (e.g. within 15 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.

#### *A Marine Structure*

The present invention also provides a marine structure comprising on at least a part of the 20 outer surface thereof an outermost fouling control coating prepared from a coating composition as defined hereinabove. In particular, at least as part of the outer surface carrying the outermost coating is a submerged part of said structure.

The coating composition, the method of establishing the coating on the substrate surface, and the characteristics of the coating follow the directions given hereinabove.

25 In one embodiment, the fouling control coating system of the marine structure may consist of an anticorrosive layer, a tie-coat and the fouling control coating as described herein.

In an alternative embodiment, the fouling control coating composition is applied on top of a used fouling control coating system, e.g. on top of a used polysiloxane-based fouling control coat.

In one particular embodiment of the above marine structure, the anticorrosive layer has a total dry film thickness of 100-600 µm, such as 150-450 µm, e.g. 200-400 µm; the tie-coat has a total dry film thickness of 50-500 µm, such as 50-400 µm, e.g. 75-350 µm or 75-300 µm or 75-250 µm; and the fouling control coating has a total dry film thickness of 20-500

5 µm, such as 20-400 µm, e.g. 50-300 µm.

A further embodiment of the marine structure is that where at least a part of the outermost surface of said structure is coated with a paint system comprising

a total dry film thickness of 150-400 µm of an anticorrosive layer of an epoxy-based coating established by application of 1-4, such as 2-4, layers;

10 a total dry film thickness of 20-400 µm of the tie-coat established by application of 1-2 layers; and

a total dry film thickness of 20-400 µm of the fouling control coating established by application of 1-2 layers.

In another embodiment of the above marine structure, the fouling control coating is applied

15 directly on the anticorrosive layer without the use of tie-coat.

*Use for improving the antifouling properties of a polysiloxane based coating composition*

The invention further relates to the use of the combination of one or more polysiloxane components modified with hydrophilic oligomer/polymer moieties and one or more biocides, wherein the weight ratio between the hydrophilic oligomer/polymer moieties and the one or

20 more biocides is in the range 1:0.02 to 1:20, for improving the antifouling properties of a polysiloxane based coating composition. The combination is particularly relevant for improving the antifouling properties against slime and algae.

It should be understood that the types of the polysiloxanes modified with hydrophilic oligomer/polymer moieties, the biocides, and the types of suitable polysiloxane based binder

25 systems are as defined further above, just at the amounts and relative proportions of the various ingredients are as defined further above.

*General Remarks*

Although the present description and claims occasionally refer to a polysiloxane, etc., it should be understood that the coating compositions defined herein may comprise one, two or

more types of the individual constituents. In such embodiments, the total amount of the respective constituent should correspond to the amount defined above for the individual constituent.

The "(s)" in the expressions: compound(s), polysiloxane(s), agent(s), etc. indicates that one,

5 two or more types of the individual constituents may be present.

On the other hand, when the expression "one" is used, only one (1) of the respective constituent is present.

## EXAMPLES

### *Materials*

10 RF-5000, ex. Shin-Etsu – Japan, silanol-terminated polydimethylsiloxane  
Xylene from local supplier  
Toluene from local supplier  
Bayferrox 130M, ex. Lanxess – Germany, Iron oxide  
Aerosil R8200, ex. Evonik Industries – Germany, Hexamethyldisilazane treated fumed silica

15 DC550, ex. Dow Corning – USA, non-reactive methylphenyl polysiloxane  
DC190, ex. Dow Corning – USA, non-reactive polyether modified polysiloxane  
Copper Omadine, ex. Arch Chemicals Inc. – Ireland, Copper Pyrithione  
SEA-NINE™ CR2 Marine Antifouling Agent, ex. Dow Microbial Control – USA, encapsulated  
DCOIT

20 Sea-Nine™ 211N, ex. Dow Microbial Control – China, DCOIT  
Silikat TES 40 WN, ex. Wacker Chemie – Germany, Ethyl silicate  
Neostann U-12, ex. Nitto Kasai – Japan, Dibutyltin Dilaurate  
Acetylacetone, ex. Wacker Chemie – Germany, 2,4-pentanedione  
Dynasylan VTMO, ex. Evonik Industries – Germany, vinyltrimethoxysilane

25 Platinum – divinyltetramethylidisiloxane complex in xylene – 2.1-2.4% platinum  
concentration, CAS No. 68478-92-2  
Polydimethylsiloxane, hydride terminated - MW<sub>n</sub> = 1100, eq. weight = 550 g/eq  
Methylhydrosiloxane – dimethylsiloxane copolymer, hydride terminated – MW<sub>n</sub> = 2300, eq.  
weight = 200 g/eq

30 Polyethylene glycol di allyl ether – MW<sub>n</sub> = 300g/mol, Eq. weight = 150 g/eq  
Polyethylene glycol mono allyl ether (hydroxyl terminated) – MW<sub>n</sub> = 350 g/mol, eq. weight =  
350 g/eq

Polyethylene glycol mono allyl ether (hydroxyl terminated) - MW<sub>n</sub> = 500 g/mol, eq. weight = 500 g/eq

*Viscosity*

In the present application with claims, viscosity is measured at 25 °C in accordance with ISO

5 2555:1989.

*Preparation method for the model paints*

Pendant hydrophilic modified polysiloxane (HMP1):

A pendant, curable poly(ethylene glycol) modified polysiloxane is prepared by mixing 25.0 g (polydimethylsiloxane-methylhydrosiloxane, hydride terminated) dissolved in 50.0 g water

10 free toluene, with 0.013 g of a solution of platinum-divinyltetramethyldisiloxane complex in xylene in a three necked flask with reflux and a continuous flow of dry nitrogen gas to keep the reaction atmosphere moisture free. A magnetic stirrer is used in the reaction flask to keep the solution agitated during the synthesis. The solution is heated to 80°C. To this solution, 11.0 g of (vinyltrimethoxysilane) is added dropwise and allowed to react for 1 h at 15 80°C. After the completion of the reaction, 54.5 g polyethylene glycol mono allyl ether is added dropwise, and allowed to react for 4h at 80°C. The solvent was hereafter partially removed under reduced pressure using a rotary evaporator until the solvent content reached 10% to obtain the final product HMP1. The content of PEG-modified PDMS binder in HMP1 is 90 % w/w. The amount of PEG in the HMP1 binder is 60.2% w/w calculated on dry weight.

20 Linear hydrophilic modified polysiloxane (HMP2):

A linear, curable poly(ethylene glycol) modified polysiloxane is prepared by mixing 5.00 g (polyethylene glycol diallyl ether) dissolved in 50.0 g water free toluene, with 0.013 g of a solution of platinum–divinyltetramethyldisiloxane complex in xylene in a three necked flask with reflux and a continuous flow of dry nitrogen gas to keep the reaction atmosphere

25 moisture free. A magnetic stirrer is used in the reaction flask to keep the solution agitated during the synthesis. The solution is heated to 65°C. To this solution, 65.0 g polydimethylsiloxane (hydride terminated) is added dropwise, and allowed to react for 1 h at 80°C. After the completion of the reaction, 35.0 g of vinyltrimethoxysilane is added dropwise at 80°C and allowed to react for 1 h at 80°C. The solvent was hereafter partially removed

under reduced pressure using a rotary evaporator until the solvent content reached 10% to obtain the final product HMP2. The content of PEG-modified PDMS binder in HMP2 is 90 % w/w. The amount of PEG in the HMP2 binder is 4.8% w/w calculated on dry weight.

Pendant hydrophilic modified polysiloxane (HMP3):

5 A pendant, curable poly(ethylene glycol) modified polysiloxane is prepared by mixing 25.0 g polydimethylsiloxane-methylhydrosiloxane, hydride terminated dissolved in 50.0 g water free toluene, with 0.14 g platinum – divinyltetramethyldisiloxane complex in xylene solution. The solution is heated to 80°C. To this solution, 4.0 g of vinyltrimethoxysilane is added dropwise and allowed to react for 1/2h at 80°C. After the completion of the reaction, 68.5 g  
10 polyethylene glycol mono allyl ether [A350] is added drop wise, and allowed to react for 3h at 80°C. The content of PEG-modified PDMS binder in HMP3 is 66.1 % w/w. The amount of PEG in the HMP3 binder is 70.3% w/w calculated on dry weight.

Linear hydrophilic modified polysiloxane (HMP4):

15 A linear, curable poly(ethylene glycol) modified polysiloxane is prepared by mixing 100.0 g of hydride terminated polydimethylsiloxane dissolved in 75.0 g water free toluene, with 0.17 g of platinum – divinyltetramethyldisiloxane complex in xylene solution. The solution is heated to 80°C under stirring. To this solution 1.7 g polyethylene glycol di allyl ether [AA300] is added dropwise, and allowed to react for 2h at 80°C. After the completion of the reaction 5.4 g of vinyltrimethoxysilane is added dropwise at 80°C and allowed to react for 1h at 80°C. The  
20 content of PEG-modified PDMS binder in HMP4 is 58.8 % w/w. The amount of PEG in the HMP4 binder is 1.6% w/w calculated on dry weight.

Pendant hydrophilic modified polysiloxane (HMP5):

25 A pendant, curable poly(ethylene glycol) modified polysiloxane is prepared by mixing 25.0 g polydimethylsiloxane-methylhydrosiloxane, hydride terminated dissolved in 50.0 g water free toluene, with 0.14 g platinum – divinyltetramethyldisiloxane complex in xylene solution. The solution is heated to 80°C. To this solution, 4.0 g of vinyltrimethoxysilane is added dropwise and allowed to react for 1/2h at 80°C. After the completion of the reaction, 90.0 g polyethylene glycol mono allyl ether [A500] is added dropwise, and allowed to react for 3h at 80°C. The content of PEG-modified PDMS binder in HMP5 is 70.4 % w/w. The amount of PEG  
30 in the HMP5 binder is 75.6% w/w calculated on dry weight.

Compositions A to Z:

Part (i) silanol-terminated polydimethylsiloxane, xylene, silica, polyamide wax, red iron oxide, (biocide) are mixed on a Diaf dissolver equipped with an impeller disc (70 mm in diameter) in a 1 L can for 15 minutes at 2000 rpm.

- 5 Part (ii) ethyl silicate, (xylene), catalyst, 2,4-pentanedione, (non-reactive hydrophilic modified polysiloxane oil), (phenyl methyl polysiloxane)) are mixed on a Diaf dissolver equipped with an impeller disc (70 mm in diameter) in a 1 L can for 2 minutes at 500 rpm.
  
- Part (iii) (Reactive hydrophilic modified polysiloxane) the container is closed under dry nitrogen to avoid moisture.
  
- 10 Before the application, part (i), part (ii) and part (iii) are mixed to a homogenous mixture.

*Test Methods*Blister Box Test

- 15 The Blister Box test is used to determine the influence of polysiloxanes modified with hydrophilic oligomer/polymer moieties on the stability of the PDMS coating to which they are added to.

*Preparation of panels*

- 20 Steel panels (150x75x15 mm) are coated with 100 µm (dry film thickness, DFT) of a commercial epoxy primer (HEMPADUR Quattro 17634) applied by airless spraying. After 12 - 48 hrs of drying at room temperature a silicone tie coat (HEMPASIL Nexus 27302) is applied by doctor blade of 300 µm clearance. After 16-30 hrs of drying the top coat paint compositions are applied by doctor blade of 400 µm clearance. The panels are dried for 24 hrs before testing in the blister box.

*Testing*

- 25 The panel surface with the coating system is exposed to 40 °C, saturated water vapour, at an angle of 15°/60° to the horizontal. The reverse side of the panel is exposed to room

temperature. At the selected inspection intervals during and after completion of exposure, adhesion between tie coat/top coat and general condition of the top coat are evaluated.

Evaluation of adhesion between tie coat and top coat is based on the below ranking:

	Adhesion	Ranking Value
5	FAIL/POOR	No adhesion/poor adhesion
	GOOD	Acceptable adhesion

Panels are exposed for two months and typically checked every week.

### Raft Test

#### *Preparation of panels*

10 An acrylic panel (150x200 mm), sandblasted on one side to facilitate adhesion of the coating, is coated with 100 µm (DFT) of a commercial epoxy (HEMPEL Light Primer 45551) applied by air spraying. After 6 – 24 hrs of drying at room temperature a tie coat is applied by doctor blade of 300 µm clearance. After 16-30 hrs of drying the top coat paint compositions are applied by doctor blade of 400 µm clearance. The panels are dried for at least 72 hrs before  
 15 immersion on the raft.

#### *Testing*

Panels are tested at two different locations; Spain and Singapore.

#### Test site in Spain

20 Located in Vilanova in north-eastern Spain. At this test site the panels are immersed into sea water with salinity in the range of 37-38 parts per thousand at an average temperature of 17-18 °C.

#### Test site in Singapore

At this test site the panels are immersed into sea water with salinity in the range of 29-31 parts per thousand at a temperature in the range of 29-31 °C. Panels are inspected every 4-12 weeks and evaluated according to the following scale:

Level	Description
Excellent	Only slime
Good	Algae + Animals < 10 %
Fair	10 % < Algae + Animals < 25 %
Poor	Algae + Animals > 25 %

*Examples*

The following model paints were prepared for testing for antifouling performance.

All entries in model paints table are in weight unless otherwise stated. In the calculation of  
 5 the final polysiloxane matrix, all the hydrolysable groups are presumed completely  
 hydrolysed and reacted into a matrix through a condensation reaction with the polysiloxane  
 binder. Therefore, the ethyl silicate contributes with 41 % of its weight to the calculations of  
 the final polysiloxane matrix and vinyltrimethoxysilane contributes with 54 % of its weight  
 correspondingly. When calculating the polysiloxane content of the binder matrix, the  
 10 constituents included in the calculations as the starting materials, however with the above-  
 mentioned corrections for ethyl silicate and vinyltrimethoxysilane.

Model paints	Top coat composition A	Top coat composition B
<b>Part (i)</b>		
Silanol-terminated polydimethylsiloxane	59.1	27.1
Xylene	17.4	17.4
Thixotropic agent	2.2	2.2
Pigments	4.1	4.1
<i>Biocide:</i>		
Copper pyrithione	4.8	4.8
DCOIT		
Encapsulated DCOIT		
<b>Total part (i)</b>	87.6	55.6
<b>Part (ii)</b>		
Ethyl silicate	2.3	2.3
Xylene	3.6	3.6
Dibutyltin dilaurate	0.4	0.4
2,4-pentanedione	1.1	1.1
<b>Total part (ii)</b>	7.4	7.4
<b>Part (iii)</b>		
Pendant hydrophilic modified polysiloxane (HMP 1)	5	
Linear hydrophilic modified polysiloxane (HMP 2)		37
<b>Total part (iii)</b>	5	37
<b>Total part (i), (ii), (iii)</b>	100	100
Hydrophilic oligomer/polymer	2.71	1.59
Hydrophilic oligomer/polymer : biocide (1:x)	1.77	3.03
HMP binder in % of binder phase	6.8	53
Polysiloxane content of the binder matrix (wt%)	95.8	97.2
Performance on raft in Spain (8w)	Good	Good
Adhesion	Good	Good

*Comments:* The examples A, B illustrate the performance of the biocide containing paint compositions when the hydrophilic polymers have been incorporated in the paint matrix.

Model paints	Top coat composition C	Top coat composition D	Top coat composition E (reference)
<b>Part (i)</b>			
Silanol-terminated polydimethylsiloxane	57.1	25.1	64.1
Xylene	17.4	17.4	17.4
Thixotropic agent	2.2	2.2	2.2
Pigments	4.1	4.1	4.1
<i>Biocide:</i>			
Copper pyrithione	4.8	4.8	4.8
<b>Total part (i)</b>	85.6	53.6	92.6
<b>Part (ii)</b>			
Ethyl silicate	2.3	2.3	2.3
Non-reactive hydrophilic modified polysiloxane	2	2	
Xylene	3.6	3.6	3.6
Dibutyltin dilaurate	0.4	0.4	0.4
2,4-pentanedione	1.1	1.1	1.1
<b>Total part (ii)</b>	9.4	9.4	7.4
<b>Part (iii)</b>			
Pendant hydrophilic modified polysiloxane (HMP 1)	5		
Linear hydrophilic modified polysiloxane (HMP 2)		37	
<b>Total part (iii)</b>	5	37	0
<b>Total part (i), (ii), (iii)</b>	100	100	100
Hydrophilic oligomer/polymer	2.71	1.59	0
Hydrophilic oligomer/polymer : biocide (1:x)	1.77	3.03	-
HMP binder in % of binder phase	7.0	55	0
Polysiloxane content of the binder matrix (wt%)	95.7	97.1	100
Performance on raft in Singapore (8w)	Excellent	Excellent	Fair
Adhesion	Good	Good	Good

*Comments:* The examples C, D illustrate the influence of the addition of a hydrophilic modified polysiloxane oil in a composition with hydrophilic oligomer/polymer moieties reacted to the binder. Reference example E shows a biocide containing paint formulation without hydrophilic moieties reacted to the binder.

5 In the following examples, the coating compositions are provided in terms of the dry weight of the cured film.

Model paints	Top coat composition F	Top coat composition G (reference)
<b>Part (i)</b>		
Silanol-terminated polydimethylsiloxane	63.0	63.0
Thixotropic agent	2.9	2.9
Pigments	5.4	11.6
<i>Biocide:</i>		
Copper pyrithione	6.2	0.0
<b>Total part (i)</b>	77.5	77.5
<b>Part (ii)</b>		
Ethyl silicate	0.9	0.9
Non-reactive hydrophilic modified polysiloxane	0.0	0.0
Dibutyltin dilaurate	0.5	0.5
<b>Total part (ii)</b>	1.4	1.4
<b>Part (iii)</b>		
Pendant hydrophilic modified polysiloxane (HMP3)	21.0	21.0
<b>Total part (iii)</b>	21.0	21.0
<b>Total part (i), (ii), (iii)</b>	99.9	99.9
Hydrophilic oligomer/polymer	14.8	14.8
Hydrophilic oligomer/polymer : biocide (1:x)	0.42	0

HMP binder in % of binder phase	25	25
Polysiloxane content of the binder matrix (wt%)	82.4	82.4
Performance on raft in Spain (7w)	Excellent	Good

*Comments:* The example F and reference example G show the improvement of performance when adding biocide to a hydrophilic modified polysiloxane-based fouling release coating.

Model paints	Top coat composition H (reference)	Top coat composition I	Top coat composition F	Top coat composition J	Top coat composition K (reference)
<b>Part (i)</b>					
Silanol-terminated polydimethylsiloxane	83.7	75.5	63.0	42.1	83.7
Thixotropic agent	2.9	2.9	2.9	2.9	2.9
Pigments	5.4	5.4	5.4	5.4	11.6
<i>Biocide:</i>					
Copper pyrithione	6.2	6.2	6.2	6.2	
<b>Total part (i)</b>	98.2	90.0	77.5	56.5	98.2
<b>Part (ii)</b>					
Ethyl silicate	1.2	1.1	0.9	0.6	1.2
Non-reactive hydrophilic modified polysiloxane	0.0	0.0	0.0	0.0	0.0
Dibutyltin dilaurate	0.5	0.5	0.5	0.5	0.5
<b>Total part (ii)</b>	1.7	1.6	1.4	1.2	1.7
<b>Part (iii)</b>					
Pendant hydrophilic modified polysiloxane (HMP3)		8.4	21.0	42.1	
<b>Total part (iii)</b>		8.4	21.0	42.1	
<b>Total part (i), (ii), (iii)</b>	99.9	100.1	99.9	99.8	99.9

Hydrophilic oligomer/polymer	0	5.9	14.8	29.6	
Hydrophilic oligomer/polymer : biocide (1:x)	-	1.1	0.42	0.21	
HMP binder in % of binder phase	0	10	25	50	0
Polysiloxane content of the binder matrix (wt%)	100	93.0	82.4	64.6	100
Performance on raft in Singapore (8w)	Poor	Excellent	Excellent	Excellent	Poor

*Comments:* The examples I, F and J shows the improved performance of the hydrophilic modified binder with biocide compared to biocides in a polysiloxane binder without hydrophilic moieties (reference example H) and biocide-free polysiloxane without hydrophilic moieties (reference example K).

Model paints	Top coat composition L	Top coat composition M	Top coat composition N	Top coat composition O	Top coat composition H (reference)
<b>Part (i)</b>					
Silanol-terminated polydimethylsiloxane	63.0	75.5	74.5	76.5	83.7
Thixotropic agent	2.9	2.9	2.9	2.9	2.9
Pigments	5.4	5.4	11.5	11.8	5.4
<i>Biocide:</i>					
Copper pyrithione	6.2	6.2	4.0	1.5	6.2
<b>Total part (i)</b>	77.5	90.0	92.9	92.7	98.2
<b>Part (ii)</b>					
Ethyl silicate	0.9	1.1	1.1	1.1	1.2
Non-reactive hydrophilic modified polysiloxane	0.0	0.0	0.0	0.0	0.0
Dibutyltin dilaurate	0.5	0.5	0.5	0.5	0.5
<b>Total part (ii)</b>	1.4	1.6	1.6	1.6	1.7
<b>Part (iii)</b>					

Pendant hydrophilic modified polysiloxane (HMP5)	21.0	8.4	5.5	5.6	
<b>Total part (iii)</b>	21.0	8.4	5.5	5.6	-
<b>Total part (i), (ii), (iii)</b>	99.9	100.0	100.0	99.9	99.9
Hydrophilic oligomer/polymer	15.9	6.4	4.2	4.2	0
Hydrophilic oligomer/polymer : biocide (1:x)	0.39	0.98	0.96	0.35	-
HMP binder in % of binder phase	25.0	10.0	6.8	6.8	0
Polysiloxane content of the binder matrix(wt%)	81.1	92.5	94.8	94.9	100
Performance on raft in Singapore (8w)	Excellent	Excellent	Good	Fair	Poor

*Comments:* Compositions L to O are further examples of the performance of a hydrophilic modified polysiloxane binder. Also shown in the examples L to O are the different ratios between biocide and hydrophilic oligomer/polymer that gives rise to an improved performance over the biocide-free reference shown as composition H.

Model paints	Top coat composition H (reference)	Top coat composition P	Top coat composition Q	Top coat composition R	Top coat composition K (reference)
<b>Part (i)</b>					
Silanol-terminated polydimethylsiloxane	83.7	71.6	71.6	75.5	83.7
Thixotropic agent	2.9	2.9	2.9	2.9	2.9
Pigments	5.4	5.4	5.4	5.4	11.6
<i>Biocide:</i>					
Copper pyrithione	6.2	6.2	6.2		
DCOIT				6.2	
<b>Total part (i)</b>	98.2	86.1	86.1	90.0	98.2
<b>Part (ii)</b>					
Ethyl silicate	1.2	1.1	1.1	1.1	1.2
Non-reactive hydrophilic modified polysiloxane	0.0	0.0	3.9	0.0	
Non-reactive phenyl modified polysiloxane	0.0	3.9	0.0	0.0	
Dibutyltin dilaurate	0.5	0.5	0.5	0.5	0.5

<b>Total part (ii)</b>	1.7	5.5	5.5	1.6	1.7
<b>Part (iii)</b>					
Pendant hydrophilic modified polysiloxane (HMP3)		8.4	8.4	8.4	
<b>Total part (iii)</b>		8.4	8.4	8.4	
<b>Total part (i), (ii), (iii)</b>	99.9	100.0	100.0	100.0	99.9
Hydrophilic oligomer/polymer	0	5.9	5.9	5.9	
Hydrophilic oligomer/polymer : biocide (1:x)		1.05	1.05	1.05	
HMP binder in % of binder phase	0	10.4	10.4	9.88	0
Polysiloxane content of the binder matrix (wt%)	100	92.7	92.7	93.0	100
Performance on raft in Singapore (8w)	Poor	Excellent	Excellent	Fair	Poor

*Comments:* The example R shows the effect of a different biocide in a hydrophilic modified polysiloxane binder matrix. Examples P and Q shows the effect of addition of non-reactive polysiloxane oils in a biocide containing, hydrophilic modified polysiloxane binder.

Model paints	Top coat composition H (reference)	Top coat composition S	Top coat composition T	Top coat composition U	Top coat composition V
<b>Part (i)</b>					
Silanol-terminated polydimethylsiloxane	83.7	42.1	63	41.8	42.5
Thixotropic agent	2.9	2.9	2.9	2.9	2.9
Pigments	5.4	5.4	5.4	11.6	11.8
<i>Biocide:</i>					
Copper pyrithione	6.2	6.2	6.2	4	1.5
<b>Total part (i)</b>	98.2	56.6	77.5	60.3	58.7
<b>Part (ii)</b>					
Ethyl silicate	1.2	0.6	0.9	1.1	1.1
Non-reactive hydrophilic modified polysiloxane	0.0	0.0	0.0	0.0	0.0
Dibutyltin dilaurate	0.5	0.5	0.5	0.5	0.5
<b>Total part (ii)</b>	1.7	1.1	1.4	1.6	1.6
<b>Part (iii)</b>					

Linear hydrophilic modified polysiloxane (HMP4)		42.1	21.0	38.1	39.6
<b>Total part (iii)</b>		42.1	21.0	38.1	39.6
<b>Total part (i), (ii), (iii)</b>	99.9	99.9	99.9	100.0	100.0
Hydrophilic oligomer/polymer	0	0.67	0.33	0.60	0.63
Hydrophilic oligomer/polymer : biocide (1:x)	-	9.28	18.6	6.61	2.39
HMP binder in % of binder phase	0	50.0	25.0	47.0	47.6
Polysiloxane content of the binder matrix (wt%)	100	99.2	99.6	99.2	99.2
Performance on raft in Singapore (6w)	Poor	Good	Fair	Fair	Fair

Model paints	Top coat composition X (reference)	Top coat composition Y (reference)	Top coat composition Z (reference)
<b>Part (i)</b>			
Silanol-terminated polydimethylsiloxane	83.7	42.1	63.1
Thixotropic agent	2.9	2.9	2.9
Pigments	11.6	11.6	11.6
<i>Biocide:</i>			
Copper pyrithione			
<b>Total part (i)</b>	98.2	56.7	77.6
<b>Part (ii)</b>			
Ethyl silicate	1.2	0.6	0.9
Non-reactive hydrophilic modified polysiloxane	0.0	0.0	0.0
Dibutyltin dilaurate	0.5	0.5	0.5
<b>Total part (ii)</b>	1.7	1.1	1.4
<b>Part (iii)</b>			
Linear hydrophilic modified polysiloxane (HMP4)		42.1	21.0
<b>Total part (iii)</b>		42.1	21.0

Total part (i), (ii), (iii)	99.9	100.0	100.0
Hydrophilic oligomer/polymer	0	0.67	0.33
Hydrophilic oligomer/polymer : biocide (1:x)	-	-	-
HMP binder in %t of binder phase	0	50.0	25.0
Polysiloxane content of the binder matrix (wt%)	100	99.2	99.6
Performance on raft in Singapore (8w)	Poor	Poor	Poor

Comments: The examples S, T, U and V show the performance improvement of adding biocides to an ABA type hydrophilic modified polysiloxane binder. Reference examples H and X is an unmodified polysiloxane binder composition with and without biocide, respectively. Reference examples Y and Z illustrate the performance of a linear hydrophilic modified polysiloxane without biocides.

## CLAIMS

1. A cured paint coat comprising a polysiloxane-based binder matrix and one or more biocides, said binder matrix having included as a part thereof hydrophilic oligomer/polymer moieties, wherein the weight ratio between the hydrophilic oligomer/polymer moieties and the one or more biocides is in the range 1:0.02 to 1:20, and wherein more than 50 % by weight of the binder matrix is represented by polysiloxane parts.

2. The paint coat according to claim 1, wherein the hydrophilic oligomer/polymer moieties are selected from poly(vinyl pyrrolidone), poly[N-(2-hydroxypropyl)methacrylamide], poly(acrylic acid), poly(glycerol), polyHEMA, polysaccharides, poly(vinyl alcohol), polyketones, poly(aldehyde guluronate), polyvinylamine, polycaprolactones, poly(vinyl acetate), polyoxyalkylenes like poly(ethylene glycol), poly(propylene glycol), poly(2-methyl-2-oxazoline), including copolymers of the foregoing, in particular poly(oxyalkylenes).

3. The paint coat according to claim 2, wherein the poly(oxyalkylene) is selected from polyoxyethylene, polyoxypropylene and poly(oxyethylene-co-oxypropylene).

4. The paint coat according to any one of the preceding claims, wherein at least one biocide is an organic biocide.

5. The paint coat according to any one of the preceding claims, wherein the one or more biocides constitutes 0.1-10 % by dry weight of the paint coat.

6. The paint coat according to any one of the preceding claims, wherein the weight ratio between the hydrophilic oligomer/polymer moieties and the one or more biocides is in the range 1:0.05 to 1:5.

7. A marine structure comprising on at least a part of the outer surface thereof a paint coat as defined in any one of the preceding claims.

8. The structure according to claim 7, wherein at least as part of the outer surface carrying the outermost coating is a submerged part of said structure.

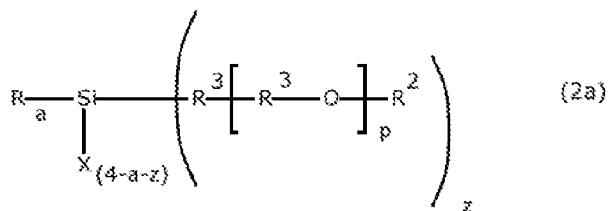
9. A fouling control coating composition comprising a polysiloxane-based binder system, said binder system comprising one or more reactive polysiloxane components modified with hydrophilic oligomer/polymer moieties, and one or more biocides, wherein the weight ratio between the hydrophilic oligomer/polymer moieties and the one or more biocides is in the

range 1:0.02 to 1:20, and wherein more than 50 % by weight of the binder system is represented by polysiloxane parts.

10. A fouling control coating composition comprising a polysiloxane-based binder system, said binder system comprising one or more hydrophilic oligomer/polymer moieties which at

5 one or both ends carry  $-\text{Si}(\text{R}^*)_3$  groups, wherein each  $\text{R}^*$  independently is selected from  $\text{C}_{1-4}$ -alkyl and  $\text{C}_{1-4}$ -alkoxy, at least one being  $\text{C}_{1-4}$ -alkoxy, and one or more biocides, wherein the weight ratio between the hydrophilic oligomer/polymer moieties and the one or more biocides is in the range 1:0.02 to 1:20, and wherein more than 50 % by weight of the binder system is represented by polysiloxane parts.

0 11. A fouling control coating composition comprising a polysiloxane-based binder system, said binder system comprising a cross-linker of formula (2a)



wherein, each R represents, independently, an unsubstituted or substituted monovalent hydrocarbon group of 1 to 6 carbon atoms or a hydrolysable group; each X represents,

5 independently, a hydrolysable group; each  $\text{R}^2$  is independently selected from -H,  $\text{C}_{1-4}$ -alkyl (e.g.  $-\text{CH}_3$ ,  $-\text{CH}_2\text{CH}_3$ ,  $-\text{CH}_2\text{CH}_2\text{CH}_3$ ,  $-\text{CH}(\text{CH}_3)_2$ ,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), phenyl ( $-\text{C}_6\text{H}_5$ ), and  $\text{C}_{1-4}$ -alkylcarbonyl (e.g.  $-\text{C}(=\text{O})\text{CH}_3$ ,  $-\text{C}(=\text{O})\text{CH}_2\text{CH}_3$  and  $-\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{CH}_3$ ), in particular -H and methyl; each  $\text{R}^3$  is independently selected from  $\text{C}_{2-5}$ -alkylene (e.g.  $-\text{CH}_2\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}(\text{CH}_3)-$ ,  $-\text{CH}_2\text{CH}_2\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)-$ ), arylene (e.g. 1,4-phenylene) and  $\text{C}_{2-5}$ -alkylene substituted with aryl (e.g. 1-phenyl ethylene), in particular from  $\text{C}_{2-5}$ -alkylene such as  $-\text{CH}_2\text{CH}_2-$  and  $-\text{CH}_2\text{CH}(\text{CH}_3)-$ ;

20  $\text{p}$  is 0-50;  $\text{a}$  is 0-2;  $\text{z}$  is 1-3; and one or more biocides, wherein the weight ratio between the groups  $-\text{R}^3-[-\text{R}^3-\text{O}-]_{\text{p}}-\text{R}^2$  in formula (2a) and the one or more biocides is in the range 1:0.02 to 1:20, and wherein more than 50 % by weight of the binder system is represented by polysiloxane parts.

25 12. The coating composition according to any one of the claims 9 and 10, wherein the hydrophilic oligomer/polymer moieties are selected from poly(vinyl pyrrolidone), poly[N-(2-hydroxypropyl)methacrylamide], poly(acrylic acid), poly(glycerol), polyHEMA, polysaccharides, poly(vinyl alcohol), polyketones, poly(aldehyde guluronate), polyvinylamine,

polycaprolactones, poly(vinyl acetate), polyoxyalkylenes like poly(ethylene glycol), poly(propylene glycol), poly(2-methyl-2-oxazoline), including copolymers of the foregoing, in particular poly(oxyalkylenes).

13. The coating composition according to claim 11, wherein the groups  $-R^3-[-R^3-O-]_p-R^2$  in formula (2a) are selected from polyoxyethylene, polyoxypropylene and poly(oxyethylene-co-oxypropylene).

14. The coating composition according to claims 12, wherein the poly(oxyalkylene) is selected from polyoxyethylene, polyoxypropylene and poly(oxyethylene-co-oxypropylene).

15. The coating composition according to any one of the claims 9-14, wherein at least one biocide is an organic biocide.

16. The coating composition according to any one of the claims 9-15, wherein the weight ratio between the hydrophilic oligomer/polymer moieties and the one or more biocides is in the range 1:0.05 to 1:5.

17. Use of the combination of one or more reactive polysiloxane components modified with hydrophilic oligomer/polymer moieties and one or more biocides, wherein the weight ratio between the hydrophilic oligomer/polymer moieties and the one or more biocides is in the range 1:0.02 to 1:20, for improving the antifouling properties of a polysiloxane based coating composition.