

NOVEL 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 fouling surface. The traditional polydimethylsiloxane (PDMS) coatings have shown difficulty in resisting slime fouling over time, thus decreasing the advantage of drag reduction.

10 Hence, there is a need for fouling control polysiloxane-based coating compositions combining 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.

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

5 WO 2002/088043 discloses a process for coating a siliceous substrate with a silicon-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 polyethylene glycol or polypropylene glycol moieties. It is further envisaged, that antifouling agents may be used, in particular copper and inorganic copper compounds.

10 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 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 certain reactive silanes, and which further comprises, e.g., an poly(oxyalkylene)-modified polysiloxane. The composition may also include an antifouling agent.

The silicone based fouling release coatings have demonstrated an advantage over conventional antifouling coatings showing significant lower drag resistance, hence reduced 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.

Some traditional biocide containing antifouling coatings have demonstrated a greater resistance towards marine fouling compared to the silicone based fouling release coatings under, e.g., static 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 that will remain fouling free for a longer time than conventional silicone based fouling release coatings.

SUMMARY

In view of the above-mentioned needs, the present inventors have now developed new fouling control coating compositions which comprise biocides and one or more hydrophilic-modified polysiloxanes which facilitate and control 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.

The present inventors have realised that the use of certain hydrophilic-modified polysiloxanes, in particular poly(oxyalkylene)-modified polysiloxanes, (see further below) renders it possible to obtain a media for water- and biocidal transport through a cross-linked polysiloxane film, in particular a film of a polysiloxane-based coating composition. The leach rate of the biocide can be controlled amongst others by the amount and the hydrophilicity/hydrophilic moieties of the added polysiloxane(s).

In a first aspect, there is provided a fouling control coating composition comprising a polysiloxane-based binder system,
0.01-20 % by dry weight of one or more hydrophilic-modified polysiloxanes, and one or more biocides, wherein the weight ratio between the one or more hydrophilic-modified polysiloxanes and the one or more biocides is in the range 1:0.2 to 1:6, wherein the hydrophilic-modified polysiloxane has a number average molecular weight (M_n) in the range of 100-100,000 g/mol, and wherein the one or more hydrophilic-modified polysiloxanes do not contain groups that can react with the binder or any cross-linker.

In a second aspect, there is provided a top coat composition as defined above which comprises:

- (i) 40-70 % by wet weight of the total top coat composition of a silanol-terminated polydiorganosiloxane and a cross-linker;
- (ii) 0.1-10 % by wet weight of the total top coat composition of one or more biocides, preferably selected from organic biocides; and
- (iii) 0.1-10 % by wet weight of the total top coat composition of one or more hydrophilic-modified polysiloxanes selected from poly(oxyalkylene)-modified polysiloxanes with the proviso that the weight ratio between the one or more poly(oxyalkylene)-modified polysiloxanes and the one or more biocides is in the range 1:0.2 to 1:6.

In a third aspect, there is provided a marine structure comprising on at least a part of the outer surface thereof an outermost coating prepared from a coating composition as defined above.

In a fourth aspect, there is provided the use of the combination of one or more non-reactive hydrophilic-modified polysiloxanes and one or more biocides, wherein the weight ratio between the one or more hydrophilic-modified polysiloxanes and the one or more biocides is in the range 1:0.2 to 1:6, wherein the hydrophilic-modified polysiloxane has a number average molecular weight (M_n) in the range of 100-100,000 g/mol, and wherein the one or more hydrophilic-modified polysiloxanes do not contain groups that can react with the binder or any cross-linker, for improving the antifouling properties of a polysiloxane based coating composition.

So, in a first embodiment the present disclosure relates to a fouling control coating composition comprising a polysiloxane-based binder system, 0.01-20 % by dry weight of one or more hydrophilic-modified polysiloxanes, and one or more biocides.

A second embodiment of the disclosure relates to a marine structure comprising on at least a part of the outer surface thereof an outermost coating prepared from a coating composition as defined herein.

In currently preferred embodiments of the above aspects, the weight ratio between the one or more hydrophilic-modified polysiloxanes and the one or more biocides is in the range 1:0.2 to 1:6.

5 A third embodiment of the disclosure relates to the use of the combination of one or more non-reactive hydrophilic-modified polysiloxanes and one or more biocides, wherein the weight ratio between the one or more hydrophilic modified polysiloxanes and the one or more biocides is in the range 1:0.2 to 1:6, for improving the antifouling properties of a polysiloxane based coating composition.

DETAILED DISCLOSURE OF THE INVENTION

10 *The coating composition*

As mentioned above, the present invention provides a fouling control coating composition comprising a polysiloxane-based binder system 0.01-20 %, e.g. 0.05-10 %, by dry weight of one or more hydrophilic-modified polysiloxanes, and one or more biocides.

Hydrophilic-modified polysiloxane

15 Hydrophilic-modified polysiloxanes are widely used as surfactants and emulsifiers due to the content of both hydrophilic and lipophilic groups in the same molecule.

Means to obtain the hydrophilic character include modification of the polysiloxane backbone by the addition of non-ionic oligomeric or polymeric groups which can be charge-polarized 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, polysaccharides), ketones (polyketones), aldehydes (e.g. poly(aldehyde guluronate), amines (e.g. polyvinylamine), esters (e.g. polycaprolactones, poly(vinyl acetate), polyacrylates), ethers (e.g. polyoxyalkylenes like polyethylene glycol, polypropylene 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.

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It should of course be understood that the hydrophilic oligomers/polymers with which the polysiloxane component(s) 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 5-1,000 repeating units, such as 5-200, or 8-150, or 10-100 repeating units.

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 200-30,000 g/mol, in particular in the range of 300-20,000 g/mol, or in the range of 400-10,000 g/mol.

In the present description with claims, the term "hydrophilic-modified" in the context of "hydrophilic-modified polysiloxane" 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 demineralised water at 25°C.

Of particular interest are those hydrophilic-modified polysiloxanes 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.

The function of the hydrophilic-modified polysiloxane is to facilitate the dissolution and transport of the biocide to the surface. Potentially, the 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. The hydrophilic-modified polysiloxane does not contain groups that can react with the binder or the cross-linker (if present), hence the hydrophilic-modified polysiloxane is intended to be non-reactive, in particular with respect to the binder components.

The ways to control the leach rate include the molecule size of the hydrophilic-modified polysiloxane, the hydrophilicity and the miscibility with the binder. A very small molecule tends to allow a high leach rate of the biocide, while too large a molecule may not allow the leaching of the biocide to be of the desired rate. It is additionally hypothesized that the ability of the hydrophilic polysiloxanes to form a hydrated layer at the coating-water interphase is also important for this invention. In this respect, the diffusion rates of the hydrophilic polysiloxanes in the paint matrix, their relative partitioning between polysiloxane matrix and

water, the hydrophilic/hydrophobic balance, their interaction with the chosen biocide(s), and the hydration capacity of the hydrophilic substituents influence the final performance.

Hence, in a preferred embodiment, the hydrophilic-modified polysiloxane 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.

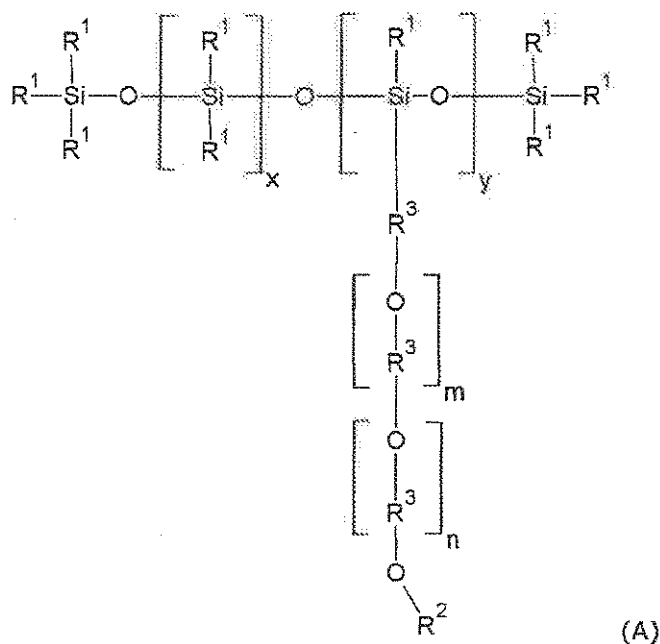
It is also preferred if the hydrophilic-modified polysiloxane has a viscosity in the range of 10-20,000 mPa·s, such as in the range of 20-10,000 mPa·s, in particular in the range of 40-5,000 mPa·s.

In the same way, a high hydrophilicity, for example due to a high concentration of hydrophilic groups such as polyethylene oxide in the molecule, could lead to an early depletion of the biocide(s) due to a high leaching rate. A combination of hydrophilic-modified polysiloxanes with different molecular weights and/or hydrophilicity may be utilized to control the leaching of the biocide.

The hydrophilic-modified polysiloxanes are devoid of any silicon-reactive groups such as Si-OH groups, hydrolysable groups such as Si-OR (alkoxy) groups, etc., so as to avoid reaction with constituents of the polysiloxane-based binder system. Otherwise the hydrophilic-modified polysiloxane may be completely integrated into the polysiloxane binder network, which is undesirable for the purpose of obtaining the technical effect on which the present invention relies.

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

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



(A)

wherein

each R¹ is independently selected from C₁₋₅-alkyl (including linear or branched hydrocarbon groups) and aryl (e.g. phenyl (-C₆H₅)), in particular methyl;

- 5 each R² is independently selected from -H, C₁₋₄-alkyl (e.g. -CH₃, -CH₂CH₃, -CH₂CH₂CH₃, -CH(CH₃)₂, -CH₂CH₂CH₂CH₃), phenyl (-C₆H₅), and C₁₋₄-alkylcarbonyl (e.g. -C(=O)CH₃, -C(=O)CH₂CH₃ and -C(=O)CH₂CH₂CH₃), in particular -H and methyl;

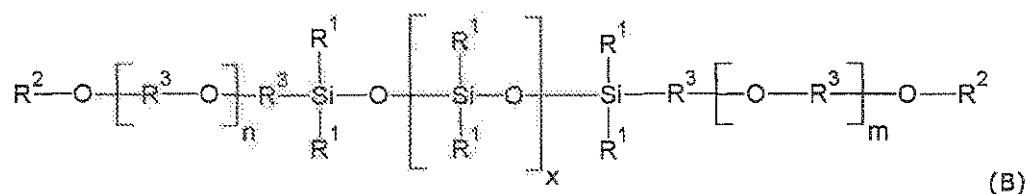
- each R³ is independently selected from C₂₋₅-alkylene (e.g. -CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH₂CH₂-, -CH₂CH₂CH₂CH₂-, -CH₂CH(CH₂CH₃)-, arylene (e.g. 1,4-phenylene) and C₂₋₅-alkylene substituted with aryl (e.g. 1-phenyl ethylene), in particular from C₂₋₅-alkylene such as -CH₂CH₂- and -CH₂CH(CH₃)-);

x is 0-2000, 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 polysiloxanes 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 is a polysiloxane having incorporated in the backbone thereof poly(oxyalkylene) chains. An illustrative example of the structure of such hydrophilic-modified polysiloxanes is formula (B):



5 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. $-CH_3$, $-CH_2CH_3$, $-CH_2CH_2CH_3$, $-CH(CH_3)_2$, $-CH_2CH_2CH_2CH_3$), 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;

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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 $-CH_2CH_2-$ and $-CH_2CH(CH_3)-$;

15 x is 0-2500; and

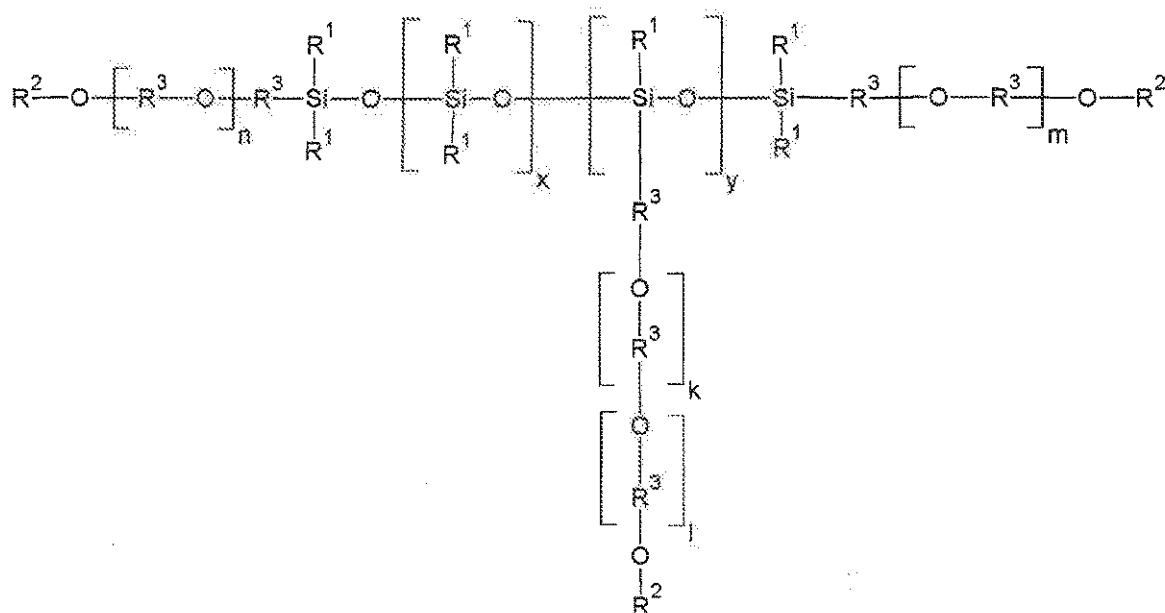
n is 0-50, m is 0-50 and $m+n$ is 1-50.

Commercially available hydrophilic-modified polysiloxanes of this type are DC 2-8692 (Dow Corning, DC Q4-3669 (Dow Corning), and DC Q4-3667 (Dow Corning).

In still another variant hereof, the poly(oxyalkylene)-modified polysiloxane 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 hydrophilic-modified polysiloxanes is formula (C):

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(C)

wherein

each R¹ is independently selected from C₁₋₅-alkyl (including linear or branched hydrocarbon groups) and aryl (e.g. phenyl (-C₆H₅)), in particular methyl;

each R² is independently selected from -H, C₁₋₄-alkyl (e.g. -CH₃, -CH₂CH₃, -CH₂CH₂CH₃, -CH(CH₃)₂, -CH₂CH₂CH₂CH₃), phenyl (-C₆H₅), and C₁₋₄-alkylcarbonyl (e.g. -C(=O)CH₃, -C(=O)CH₂CH₃ and -C(=O)CH₂CH₂CH₃), 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 $-CH_2CH_2-$ and $-CH_2CH(CH_3)-$;

x is 0-2000, 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

15 n is 0-50, m is 0-50 and $m+n$ is 1-50.

In the above structures (A), (B) and (C), the groups $-\text{CH}_2\text{CH}(\text{CH}_3)-$, $-\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)-$, 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 in the polysiloxane structure.

In these embodiments and variants, the poly(oxyalkylene) is preferably selected from polyoxyethylene, polyoxypropylene and poly(oxyethylene-co-oxypropylene), which
5 sometimes are referred to as polyethylene glycol, polypropylene glycol and poly(ethylene glycol-co-propylene glycol). Hence, in the above structures (A), (B) and (C), each R³ linking two oxygen atoms is preferably selected from -CH₂CH₂- and -CH₂CH(CH₃)-, whereas each R³ linking a silicon atom and an oxygen atom preferably is selected from C₂₋₅-alkyl.

In some embodiments of the above structures (A), (B) and (C), R² is preferably not
10 hydrogen. Other examples of hydrophilic-modified polysiloxanes are polysiloxanes modified with carbinol groups or N-pyrrolidone carboxylate copolymers or polyglycerin. It should be understood that the one or more hydrophilic-modified polysiloxanes may be of different types, e.g. two or more of the types described above.

Commercially available examples of hydrophilic-modified polysiloxanes are CMS-222 and
15 YBD-125, both ex. Gelest, USA, and KF-6100 and KF-6104, both ex. Shin-Etsu, Japan.

In some interesting embodiments, the hydrophilic-modified polysiloxane is a hydrophilic polysiloxane.

The term "hydrophilic polysiloxane" is intended to mean that the polysiloxane has been designed so as to be relatively *more* hydrophilic than a corresponding straight-chain methyl-
20 terminated polysiloxane (i.e. polydimethylsiloxane; PDMS) having the same number of silicon atoms. The relative hydrophilicity is preferably determined in accordance with the Hydrophilicity Test described in the Experimental section.

The one or more hydrophilic-modified polysiloxanes 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
25 more hydrophilic-modified polysiloxanes 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 polysiloxanes 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.

Biocides

The coating composition also includes a biocide.

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.

Illustrative examples of biocides are those selected from metallo-dithiocarbamates such as bis(dimethyldithiocarbamato)zinc, ethylene-bis(dithiocarbamato)zinc, ethylene-bis(dithiocarbamato)manganese, and complexes between these; bis(1-hydroxy-2(1H)-pyridine-thionato-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 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 compounds such as 2-(4-thiazolyl)benzimidazole, 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one, 4,5-dichloro-2-octyl-3(2H)-isothiazoline (Sea-Nine®-211N), 1,2-benzisothiazolin-3-one, and 2-(thiocyanatomethylthio)-benzothiazole; urea derivatives such as N-(1,3-bis(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 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-nitrilo-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-didecyl-N-methyl-poly(oxyethyl)ammonium propionate; amines such as dehydroabiethyamines 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-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.

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-tetrachloroisophthalonitrile (Chlorothalonil), copper thiocyanate (cuprous sulfocyanate), N-dichloro-fluoromethylthio-N',N'-dimethyl-N-phenylsulfamide (Dichlofluanid), 3-(3,4-dichlorophenyl)-
 5 1,1-dimethylurea (Diuron), 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile, (2-(p-chlorophenyl)-3-cyano-4-bromo-5-trifluoromethyl pyrrole; Tralopyril), N²-tert-butyl-N⁴-cyclopropyl-6-methylthio-1,3,5-triazine-2,4-diamine (Cybutryne), (RS)-4-[1-(2,3-dimethylphenyl)ethyl]-3H-imidazole (Medetomidine), 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT, Sea-Nine[®] 211N), dichlor-N-((dimethylamino)sulfonyl)fluor-N-(p-tolyl)methansulfenamid (Tolylfluanid), 2-(thiocyanomethylthio)-1,3-benzothiazole ((2-benzothiazolythio)methyl thiocyanate; TCMTB), triphenylborane pyridine (TPBP); bis(1-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), zinc ethylene-1,2-bis-dithiocarbamate (zinc-ethylene-N-N'-dithiocarbamate;
 10 Zineb) and diiodomethyl-p-tolylsulfone; Amical 48. Preferably at least one 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 3-(3,4-dichlorophenyl)-1,1-dimethylurea (Diuron), N²-tert-butyl-N⁴-cyclopropyl-6-methylthio-1,3,5-triazine-2,4-diamine (Cybutryne), 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT, Sea-Nine[®] 211N), bis(1-hydroxy-2(1H)-pyridinethionato-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).
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25 In a further particularly preferred embodiment, the biocide is an organic biocide, such as a pyrithione complex, such as zinc pyrithione. Organic biocides are those either fully or in part being of organic origin.

As detailed in US 7,377,968, in those instances in which the biocide is depleted rapidly from the film due to e.g. a high water solubility or a high level of immiscibility with the matrix composition, it can be advantageous to add one or more of the biocide(s) in encapsulated form as a means of controlling the biocide dosage and extending the effective lifetime in the film. Encapsulated biocides can also be added if the free biocide alters the properties of the polysiloxane matrix in a way that is detrimental for its use as antifouling coatings (e.g. mechanical integrity, drying times, etc.)
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In a particularly preferred embodiment, the biocide is encapsulated 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT, Sea-Nine® CR2).

In another particularly preferred embodiment, the biocide is selected from zinc pyrithione, copper pyrithione, and 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT, Sea-Nine® 211N).

- 5 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 0.1-10 % by dry weight, e.g. 0.5-8 % by dry weight, in particular 1-6 % by dry weight, of the coating composition.

- 10 The relative weight ratio between the one or more hydrophilic-modified polysiloxanes and the one or more biocides is typically in the range of 1:0.05 to 1:1000, e.g. 1:0.1 to 1:120, such as 1:0.1 to 1:10, or 1:0.15 to 1:8, in particular 1:0.2 to 1:6, or 1:0.2 to 1:5, or 1:0.25 to 1:4, especially 1:0.3 to 1:3.

Polysiloxane-based binder system

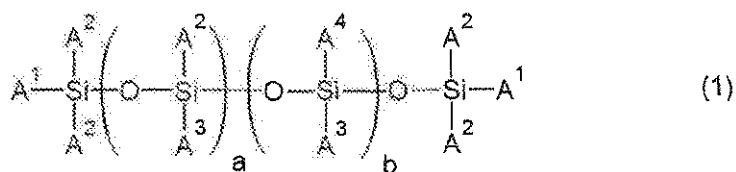
- 15 The fouling control coating composition of the invention has included therein a polysiloxane-based binder system. The binder system forms a cross-linked matrix which includes the biocide(s) and the hydrophilic-modified polysiloxane as well as other constituents such as solvents, additives, pigments, fillers, etc.

- 20 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 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
25 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 combination with a condensation reaction. In such cases, the organopolysiloxane can have
30 terminal groups of epoxy or amine and pendant hydrolysable groups, for example with alkoxy functionality.

In some embodiments, the fouling control coating composition including the polysiloxane-based binder system may be a reaction-curable composition or a moisture-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 hydroxyl-reactive polydiorganosiloxane and a silane with hydrolysable groups, or a one-component moisture-curable composition based on a polydiorganosiloxane with alkoxy or other hydrolysable reactivity.

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 is e.g. a curable diorganopolysiloxane represented by a general formula (1) shown below:



wherein

each A^1 is independently selected from a hydroxyl group, a hydrolysable group and another functional group, such as amine or epoxy;

each A^2 is independently selected from alkyl, aryl, alkenyl and a hydrolysable group;

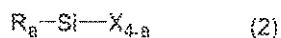
each A^3 and A^4 is independently selected from alkyl and aryl alkenyl;

$a = 1-25,000$, $b = 1-2,500$ and $a+b$ is at least 30;

The binders can be used alone or in combination. In a preferred embodiment only one generic type of the binder is used.

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:



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

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.

Preferred cross-linkers are those selected from tetraethoxysilane; vinyltris(methylethyloximo)silane; methyltris(methylethyloximo)silane; vinyltrimethoxysilane; methyltrimethoxysilane and vinyltriisopropenoxysilane; as well as hydrolysis-condensation products of the same.

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

The polysiloxane-based binder system typically constitutes at least 40 % by dry weight, in particular 50-90 % by dry weight, of the coating composition.

Catalyst

The coating composition 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 tin diacetate, dibutyl tin dioctoate, dibutyl tin 2-ethylhexoate, dioctyl tin dilaurate, dioctyl tin diacetate, dioctyl tin dioctoate, dioctyl tin 2-ethylhexoate, dioctyltin di neodecanoate, tin naphthenate, tin butyrate, tin oleate, tin caprylate, iron 2-ethylhexoate, lead 2-ethyloctoate, cobalt-2-ethylhexoate, manganese 2-ethylhexoate, zinc 2-ethylhexoate, zinc naphthenate, zinc 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 tetrapropanolate; titanium tetraisopropanolate, zirconium tetrapropanolate, zirconium tetrabutanolate; chelated

titanates such as diisopropyl bis(acetylacetyl) titanate. Further 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 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 % by weight of the total combined amount of the binder (i) and cross-linking agent (ii).

Solvents, additives, pigments and fillers

The coating composition may further comprise solvents and additives.

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.

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

Examples of additives are:

- 15 (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-ethylene oxide condensates (alkylphenol ethoxylates); ethoxylated monoethanolamides of unsaturated fatty acids such as ethoxylated monoethanolamides of linoleic acid; sodium dodecyl sulfate; and soya lecithin;
 - 20 (iii) wetting agents and dispersants such as those described in M. Ash and I. Ash, "Handbook of Paint and Coating Raw Materials, Vol. 1", 1996, Gower Publ. Ltd., Great Britain, pp 821-823 and 849-851;
 - (iv) thickeners and anti-settling agents such as colloidal silica, hydrated aluminium silicate (bentonite), aluminiumtristearate, aluminiummonostearate, xanthan gum, chrysotile, pyrogenic silica, hydrogenated castor oil, organo-modified clays, polyamide waxes and polyethylene waxes; and
 - 25 (v) dyes such as 1,4-bis(butylamino)anthraquinone and other anthraquinone derivatives; toluidine dyes, etc.
- 30 Any additives typically constitute 0-30 %, such as 0-15 %, by dry weight of the coating composition.

Furthermore, the coating composition 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 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, chromium oxide, isoindoline orange, bis-acetoacet-o-tolidiole, benzimidazolone, quinaphtalone yellow, isoindoline yellow, tetrachloroisoindolinone, quinophthalone yellow.

Examples of fillers are calcium carbonate such as 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 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 %, by dry weight of the coating composition.

With the aim of facilitating easy application of the coating composition (e.g. by spray, brush or roller application techniques), the coating composition typically has a viscosity in the range of 25-25,000 mPa·s, such as in the range of 150-15,000 mPa·s, in particular in the range of 200-4000 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 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 suitable preparation method is described in the Examples.

- 5 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
- 10 amounts stated as % by dry weight of the coating composition should be understood as % by 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 coating composition

In one preferred embodiment the top coat comprises:

- 15 (i) 40-70 % by wet weight of the total top coat composition of a silanol-terminated polydiorganosiloxane and a cross-linker;
- (ii) 0.1-10 %, such as 0.5-8 %, by wet weight of the total top coat composition of one or more biocides, preferably selected from organic biocides; and
- (iii) 0.1-10 %, such as 0.5-8 %, by wet weight of the total top coat composition of one or
- 20 more hydrophilic-modified polysiloxanes selected from the poly(oxyalkylene)-modified polysiloxanes (such as corresponding to the structures presented hereinabove).

In another preferred embodiment the top coat comprises:

- (i) 40-70 % by wet weight of the total top coat composition of a silanol-terminated polydiorganosiloxane and a cross-linker;
- 25 (ii) 0.5-8 % by wet weight of the total top coat composition of one or more organic biocides; and

(iii) 0.5-8 %, by wet weight of the total top coat composition of one or more hydrophilic-modified polysiloxanes selected from the poly(oxyalkylene)-modified polysiloxanes (such as corresponding to the structures presented hereinabove),

wherein the weight ratio between the one or more hydrophilic-modified polysiloxanes and the one or more biocides is in the range 1:0.2 to 1:6. In yet another preferred embodiment, the binder in the preferred embodiments 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 by weight of hydrolysable cross-linker, such as vinyltrimethoxysilane.

10 *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" 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. 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. 75-400 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.

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 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 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.

- 5 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 μm , such as 150-450 μm , e.g. 200-400 μm . Alternatively, the substrate may carry a paint
10 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 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.

A Marine Structure

- The present invention also provides a marine structure comprising on at least a part of the 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
20 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.

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.

- 25 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 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;

5 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.

10 In another embodiment of the above marine structure, the fouling control coating is applied 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 non-reactive hydrophilic-modified polysiloxanes and one or more biocides, wherein the weight ratio between the one or more hydrophilic-modified polysiloxanes and the one or more biocides is
15 in the range 1:0.2 to 1:6, 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 non-reactive hydrophilic-modified polysiloxanes, the biocides, and the types of suitable polysiloxane based binder systems are as defined
20 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
25 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, 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.

EXAMPLE 1

Materials

- 5 RF-5000, ex. Shin-Etsu – Japan, silanol-terminated polydimethylsiloxane
Xylene from local supplier
DC200, ex. Dow Corning – USA, polydimethyl siloxane
DC5103, ex. Dow Corning – USA, polyether modified polysiloxane (siloxylated polyether)
DC550, ex. Dow Corning – USA, non-reactive methylphenyl polysiloxane
- 10 Zinc Omadine, ex. Arch Chemicals Inc. – Ireland, Zinc Pyrithione
Copper Omadine, ex. Arch Chemical Inc. – Ireland, Copper Pyrithione
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
- 15 DC190, ex. Dow Corning – USA, polyether modified polysiloxane
DBE-621, ex. Gelest – USA, Dimethylsiloxane - ethyleneoxide block copolymer
BYK331, ex. BYK – Germany, Polyether modified polydimethylsiloxane
YBD-125, ex. Gelest – USA, Dimethylsiloxane – N-pyrrolidone carboxylate copolymer
CMS-222, ex. Gelest – USA, Carbinol functional PDMS - 20% non-siloxane
- 20 Sea-Nine 211N, ex. Dow Chemicals – USA, 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one
Sea-Nine CR2, ex. Dow Chemicals – USA, encapsulated 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one
Bayferrox 130M, ex. Lanxess – Germany, Iron oxide
Aerosil R8200, ex. Evonik Industries – Germany, Hexamethyldisilazane treated fumed silica

25 *Viscosity*

In the present application with claims, viscosity is measured at 25 °C in accordance with ISO 2555:1989.

Hydrophilicity – Relative to a PDMS

Polysiloxanes which are truly more hydrophilic than the corresponding polydimethylsiloxane (PDMS) can be identified by one or all of the following tests:

A. Water-uptake

- 5 Due to its inherent hydrophobic properties, PDMS will not take up water. One experimental criterion to identify hydrophilic polysiloxanes is that their hydrophilic content should allow them to take up at least 0.1% of their own weight when immersed to demineralized water. When 99.9 parts by weight of hydrophilic polysiloxane are vigorously mixed with 0.1 parts by weight of demineralized water, the polysiloxane will dissolve, absorb or swell the water
10 resulting in no visible phase separation.

*Preparation Method for the Model Paints*Composition A, B, C, D, E:

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

Part (ii) (ethyl silicate, xylene, catalyst, 2,4-pentanedione, (methylphenyl polysiloxane)) were 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.

- 20 Before the application, part (i) and part (ii) are mixed to a homogenous mixture

*Test Methods*Blister Box Test

The Blister Box test is used to determine the influence of hydrophilic-modified polysiloxanes (hydrophilic silicone oils) on the stability of the PDMS coating to which they are added.

Preparation of Panels

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 Dr. Blade of 400 µm clearance. The panels are dried for 24 hrs before testing in the blister box.

Testing

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
FAIL/POOR	No adhesion/poor adhesion
GOOD	Acceptable adhesion

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

Examples of adhesion between the PDMS top coat and Hemptasil Nexus tie coat after addition of 5% w/w of hydrophilic-modified polysiloxanes (polyether type) to the PDMS top coat (test results from Blister Box after 3 weeks exposure):

Hydrophilic-modified polysiloxane (polyether type)	Adhesion
DC190 (Dow Corning)	GOOD
(none) (reference)	GOOD

Raft Test*Preparation of Panels*

- 5 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 Dr. Blade of 300 μm clearance. After 16-30 hrs of drying the top coat paint compositions are applied by Dr. Blade of 400 μm clearance. The panels are dried for at least 72 hrs before immersion on the raft.

Testing

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

Test site in Spain

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.

- 15 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 ever 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

All entries in model paints table are in weight unless otherwise stated.

Model paints	Top coat composition A	Top coat composition B	Top coat composition C
Part (i)			
Silanol-terminated polydimethylsiloxane (5000 cSt)	54.9	55.0	55.4
Xylene	21.1	21.1	21.1
Polydimethyl siloxane 50 cSt	1.2	1.2	1.2
Thickeners	2.1	2.1	1.7
Pigments	3.8	3.8	3.8
<i>Hydrophilic-modified polysiloxane:</i>			
Polyether modified polysiloxane (DC5103)	4.8	4.8	4.8
<i>Biocide:</i>			
Zinc pyrithione	4.8		4.8
Copper pyrithione	0.0	4.8	0.0
Total part (i)	92.7	92.8	92.8
Part (ii)			
Ethyl silicate	2.2	2.2	2.2
Xylene	3.5	3.5	3.5
Non-reactive methylphenyl polysiloxane			
Dibutyltin dilaurate	0.5	0.5	0.5
2,4-pentanedione	1.1	1.1	1.1
Total part (ii)	7.3	7.2	7.2
Total part (i) and (ii)	100.0	100.0	100.0
Performance on raft in Spain (12 months)	EXCELLENT	EXCELLENT	EXCELLENT
Performance on raft in Singapore (12 months)	EXCELLENT	EXCELLENT	EXCELLENT

Model paints	Top coat composition D (reference)	Top coat composition E (reference)	Top coat composition F (reference)
Part (i)			
Silanol-terminated polydimethylsiloxane (5000 cSt)	55.1	57.7	58.3
Xylene	21.1	22.1	22.2
Polydimethyl siloxane 50 cSt	1.2	1.2	1.2
Thickeners	2.1	2.2	1.8
Pigments	3.9	4.0	4.0
<i>Hydrophilic-modified polysiloxane:</i>			
Polyether modified polysiloxane (DC5103)		5.1	
<i>Biocide:</i>			
Zinc pyrithione			
Copper pyrithione	4.8		
Total part (i)	88.2	92.3	87.7
Part (ii)			
Ethyl silicate	2.2	2.3	2.3
Xylene	3.5	3.6	3.6
Non-reactive methylphenyl polysiloxane	4.5		4.8
Dibutyltin dilaurate	0.5	0.5	0.5
2,4-pentanedione	1.1	1.1	1.1
Total part (ii)	11.8	7.7	12.3
Total part (i) and (ii)	100.0	100.0	100.0
Performance on raft in Spain (12 months)	FAIR	FAIR	FAIR
Performance on raft in Singapore (12 months)	FAIR	POOR	GOOD

Comments to results (composition A-F):

Some biocides might be more effective against some fouling species than others. Because the fouling species vary from location to location, performance of the top coat composition may also vary. Results are therefore included from both raft locations.

The performance of the top coat compositions with biocides is increased drastically when a hydrophilic-modified polysiloxane such as a non-reactive polyether modified polysiloxane is added (composition A and B) as this secures the biocidal transport through the cross-linked PDMS coating to the surface. Biocides alone or biocides in combination with non-reactive hydrophobic polysiloxanes do not increase the performance of the top coat composition

(composition D). It is also found that the use of a non-reactive hydrophilic-modified polysiloxane alone did not provide the advantages of the combination of the non-reactive hydrophilic-modified polysiloxane and the biocide.

Model paints	Top coat composition G	Top coat composition H	Top coat composition I (reference)
Part (i)			
Silanol-terminated polydimethylsiloxane (5000 cSt)	57.2	58.6	61.0
Xylene	17.0	17.7	18.2
Thickeners	4.7	4.8	5.0
Pigments	4.0	3.8	4.2
<i>Hydrophilic-modified polysiloxane:</i>			
Polyether modified polysiloxane (DC190)	3.6		3.7
Polyether modified polysiloxane (DBE-621)		2.8	
<i>Biocide:</i>			
Copper pyrithione	6.1		
Zinc pyrithione		4.9	
Total part (i)	92.6	92.5	92.1
Part (ii)			
Ethyl silicate	2.3	2.4	2.4
Xylene	3.6	3.7	3.8
Dibutyltin dilaurate	0.4	0.4	0.4
2,4-pentanedione	1.1	1.0	1.3
Total part (ii)	7.4	7.5	7.9
Total part (i) and (ii)	100.0	100.0	100.0
Performance on raft in Spain	EXCELLENT (38 weeks)	-	POOR (38 weeks)
Performance on raft in Singapore	EXCELLENT (38 weeks)	EXCELLENT (38 weeks)	POOR (38 weeks)

5 Comments to results (compositions G-I)

Compositions G and H contain biocides, and show improved performance compared to reference (composition I) that only contain the hydrophilic-modified polysiloxane (polyether type).

Model paints	Top coat composition J	Top coat composition K	Top coat composition L (reference)
Part (i)			
Silanol-terminated polydimethylsiloxane (5000 cSt)	59.1	59.1	63.3
Xylene	17.6	17.6	18.9
Thickeners	4.8	4.8	5.2
Pigments	4.1	4.1	4.4
<i>Hydrophilic-modified polysiloxane</i>			
N-pyrrolidone carboxylate modified polysiloxane (YBD-125)	1.9		
Carbinol modified polysiloxane (CMS-222)		1.9	
<i>Biocide:</i>			
Zinc pyrithione	4.8	4.8	
Total part (i)	92.3	92.3	91.8
Part (ii)			
Ethyl silicate	2.4	2.4	2.5
Xylene	3.7	3.7	4.0
Dibutyltin dilaurate	0.4	0.4	0.4
2,4-pentanedione	1.2	1.2	1.3
Total part (ii)	7.7	7.7	8.2
Total part (i) and (ii)	100.0	100.0	100.0
Performance on raft in Spain	~	~	~
Performance on raft in Singapore	GOOD (24 weeks)	EXCELLENT (24 weeks)	FAIR (24 weeks)

Comments to results (compositions J, K and L)

- 5 It is observed that the examples of hydrophilic, non-PEG modified PDMS compounds used in compositions J and K (YBD-125 and CMS-222) shows an improved performance compared to the biocide free polysiloxane reference (composition L) after 24 weeks of static immersion in Singapore.

Model paints	Top coat composition M	Top coat composition N (reference)
Part (i)		
Silanol-terminated polydimethylsiloxane (5000 cSt)	58.8	53.0
Xylene	17.7	16.0
Thickeners	4.8	4.3
Pigments	3.8	3.4
Hydrophilic-modified polysiloxane:		
Polyether modified polysiloxane (BYK-331)	2.8	2.5
Biocide:		
Encapsulated 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (~91%w)	4.6 (4.2)	
4,5-dichloro-2-n-octyl-4-isothiazolin-3-one solution (30%w)		14.0 (4.2)
Total part (i)	92.5	93.2
Part (ii)		
Ethyl silicate	2.4	2.2
Xylene	3.7	3.3
Dibutyltin dilaurate	0.4	0.3
2,4-pentanedione	1.0	0.9
Total part (ii)	7.5	6.8
Total part (i) and (ii)	100.0	100.0
Performance on raft in Spain		
Performance on raft in Singapore	EXCELLENT (11 weeks)	GOOD (11 weeks)

Comments to results (compositions M and N):

- 5 Compositions M and N have the same concentration of the pure biocide 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one solution. It is seen that the encapsulated biocide has a better effect than the non-encapsulated biocide in N. Both compositions contained the same hydrophilic modified polysiloxane.

CLAIMS

1. A fouling control coating composition comprising a polysiloxane-based binder system, 0.01-20 % by dry weight of one or more hydrophilic-modified polysiloxanes, and one or more biocides, wherein the weight ratio between the one or more hydrophilic-modified polysiloxanes and the one or more biocides is in the range 1:0.2 to 1:6, wherein the hydrophilic-modified polysiloxane has a number average molecular weight (M_n) in the range of 100-100,000 g/mol, and wherein the one or more hydrophilic-modified polysiloxanes do not contain groups that can react with the binder or any cross-linker.
2. The coating composition according to claim 1, wherein the relative weight ratio between the one or more hydrophilic-modified polysiloxanes and the one or more biocides is 1:0.2 to 1:4.
3. The coating composition according to claim 2, wherein the relative weight ratio between the one or more hydrophilic-modified polysiloxanes and the one or more biocides is 1:0.25 to 1:4.
4. The coating composition according to any one of the preceding claims, wherein the one or more hydrophilic-modified polysiloxanes constitute 0.05-10 % by dry weight of the coating composition.
5. The coating composition according to claim 4, wherein the one or more hydrophilic-modified polysiloxanes constitute 2-7 % by dry weight of the coating composition.
6. The coating composition according to any one of the preceding claims, wherein the one or more biocides constitutes 0.1-10 % by dry weight of the coating composition.
7. The coating composition according to any one of the preceding claims, wherein at least one biocide is an organic biocide.
8. The coating composition according to claim 7, wherein the one or more biocides are selected from 3-(3,4-dichlorophenyl)-1,1-dimethylurea (Diuron), N^2 -tert-butyl- N^4 -cyclopropyl-6-methylthio-1,3,5-triazine-2,4-diamine (Cybutryne), 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT, Sea-Nine[®] 211N), bis(1-hydroxy-2(1H)-pyridinethionato-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).

9. The coating composition according to claim 8, wherein the one or more biocides are selected from zinc pyrithione, copper pyrithione, and 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT, Sea-Nine® 211N).

10. The coating composition according to any one of the claims 7-9, wherein at least one biocide is a pyrithione complex.

11. The coating composition according to any one of the claims 7-10, wherein the one or more biocides is a pyrithione complex.

12. The coating composition according to any one of the preceding claims, wherein the hydrophilic groups have a number average molecular weight (M_n) in the range of 400-10,000 g/mol.

13. The coating composition according to any one of the preceding claims, wherein the hydrophilic-modified polysiloxane has a number average molecular weight (M_n) in the range of 500-50,000 g/mol.

14. The coating composition according to any one of the preceding claims, wherein the relative weight of the hydrophilic moieties of the one or more hydrophilic-modified polysiloxanes is 10-70% of the total weight of the hydrophilic-modified polysiloxane.

15. The coating composition according to any one of the preceding claims, wherein the polysiloxane-based binder system constitutes at least 40 % by dry weight of the coating composition.

16. The coating composition according to claim 15, wherein the polysiloxane-based binder system constitutes 50-90 % by dry weight of the coating composition.

17. The coating composition according to any one of the preceding claims, wherein the polysiloxane-based binder system constitutes at least 40 % by dry weight of the coating composition, wherein the hydrophilic-modified polysiloxanes constitute 0.05-10 % by dry weight of the coating composition, said hydrophilic-modified polysiloxane being a poly(oxyalkylene)-modified polysiloxane, and wherein the one or more biocides constitutes 0.1-10 % by dry weight of the coating composition, said coating composition having a viscosity in the range of 200-4,000 mPa·s measured at 25 °C in accordance with ISO 2555:1989, and said coating composition further comprises pigments and/or fillers in an amount of 0-35 % by dry weight of the coating composition.

18. A top coat composition according to any one of the preceding claims which comprises:

(i) 40-70 % by wet weight of the total top coat composition of a silanol-terminated polydiorganosiloxane and a cross-linker;

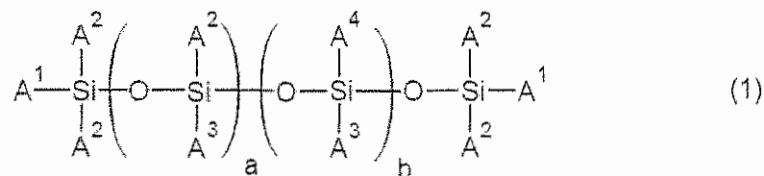
(ii) 0.1-10 % by wet weight of the total top coat composition of one or more biocides,

5 preferably selected from organic biocides; and

(iii) 0.1-10 % by wet weight of the total top coat composition of one or more hydrophilic-modified polysiloxanes selected from poly(oxyalkylene)-modified polysiloxanes with the proviso that the weight ratio between the one or more poly(oxyalkylene)-modified polysiloxanes and the one or more biocides is in the range 1:0.2 to 1:6.

10 19. The coating composition according to any one of the preceding claims, wherein the polysiloxane based binder is a functional organopolysiloxane with terminal and/or pendant functionality, said functionality either being hydrolysable groups or silanol groups.

20. The coating composition according to any one of the preceding claims, wherein the polysiloxane-based binder system comprises (i) a binder and (ii) a cross-linking agent,
15 wherein the binder (i) constitutes 20-90 % by dry weight of the coating composition, and is a curable diorganopolysiloxane represented by general formula (1):



wherein

20 each A¹ is independently selected from a hydroxyl group, a hydrolysable group, an amino group, and an epoxy group;

each A² is independently selected from alkyl, aryl, alkenyl and a hydrolysable group;

each A³ and A⁴ is independently selected from alkyl and aryl alkenyl; and

a = 1-25,000, b = 1-2,500 and a+b is at least 30.

25 21. The coating composition according to any one of the claims 19-20, wherein the organopolysiloxane has terminal groups of epoxy or amine and pendant hydrolysable groups with alkoxy functionality.

22. The coating composition according to any one of the claims 19-21, wherein said hydrolysable groups are selected from alkoxy groups and ketoxime groups.

23. The coating composition according to any one of the preceding claims, wherein the polysiloxane-based binder comprises a polydimethylsiloxane-based binder.

24. The coating composition according to any one of the preceding claims, wherein the binder system comprises a cross-linker selected from tetraethoxysilane;

5 vinyltris(methylethyloximo)silane; methyltris(methylethyloximo)silane; vinyltrimethoxysilane; methyltrimethoxysilane and vinyltrisopropenoxysilane; and hydrolysis-condensation products of the same.

25. The coating composition according to any one of the preceding claims, wherein hydrophilic character of the one or more hydrophilic-modified polysiloxanes is obtained by
10 addition of oligomeric or polymeric groups selected from amides, acids, alcohols, ketones, aldehydes, amines, esters, ethers, and imides, including copolymers thereof, said oligomeric or polymeric groups being either non-ionic or polar.

26. The coating composition according to any one of the preceding claims, wherein the hydrophilic-modified polysiloxane is a poly(oxyalkylene)-modified polysiloxane.

15 27. The coating composition according to claim 26, wherein the poly(oxyalkylene)-modified polysiloxane is a polysiloxane having grafted thereto poly(oxyalkylene) chains.

28. The coating composition according to claim 26, wherein the poly(oxyalkylene)-modified polysiloxane is a polysiloxane having incorporated in the backbone thereof poly(oxyalkylene) chains.

20 29. The coating composition according to claim 26, wherein the poly(oxyalkylene)-modified polysiloxane is a polysiloxane having incorporated in the backbone thereof poly(oxyalkylene) chains and having grafted thereto poly(oxyalkylene) chains.

30. The coating composition according to any one of the claims 17-18 and 25-29, wherein the poly(oxyalkylene) is selected from polyoxyethylene, polyoxypropylene and
25 poly(oxyethylene-co-oxypropylene).

31. A marine structure comprising on at least a part of the outer surface thereof an outermost coating prepared from a coating composition as defined in any one of the preceding claims.

32. The structure according to claim 31, wherein at least as part of the outer surface
30 carrying the outermost coating is a submerged part of said structure.

33. Use of the combination of one or more non-reactive hydrophilic-modified polysiloxanes and one or more biocides, wherein the weight ratio between the one or more hydrophilic-modified polysiloxanes and the one or more biocides is in the range 1:0.2 to 1:6, wherein the hydrophilic-modified polysiloxane has a number average molecular weight (M_n) in the range of 100-100,000 g/mol, and wherein the one or more hydrophilic-modified polysiloxanes do not contain groups that can react with the binder or any cross-linker, for improving the antifouling properties of a polysiloxane based coating composition.
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