

BIOCIDAL FOUL RELEASE COATING SYSTEMS

FIELD OF INVENTION

5 The present invention relates to the use of a foul release coating to control the leaching of biocide from a coating system comprising said foul release coating and a biocidal underlying coating. The present invention further relates to such a coating system, its use in inhibiting fouling on a substrate and a substrate coated with the coating system.

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BACKGROUND ART

Man-made marine structures such as ship and boat hulls, buoys, drilling platforms, dry dock equipment, oil production rigs, and pipes which are
15 immersed in water are prone to fouling by aquatic organisms such as green and brown algae, barnacles, mussels, and the like. Such structures are commonly of metal, but may also comprise other structural materials such as concrete. This fouling is a nuisance on boat hulls, because it increases frictional resistance during movement through the water, the consequence being reduced speeds
20 and increased fuel costs. It is a nuisance on static structures such as the legs of drilling platforms and oil production rigs, firstly because the resistance of thick layers of fouling to waves and currents can cause unpredictable and potentially dangerous stresses in the structure, and, secondly, because fouling makes it difficult to inspect the structure for defects such as stress cracking and
25 corrosion. It is a nuisance in pipes such as cooling water intakes and outlets, because the effective cross-sectional area is reduced by fouling, with the consequence that flow rates are reduced.

Fouling has been inhibited traditionally by antifouling paints containing a
30 biocide, which biocide is gradually leached from the paint. The commercially most successful methods of inhibiting fouling have involved the use of anti-

fouling coatings containing substances toxic to aquatic life, for example triorganotin compounds. Such coatings, however, are being regarded with increasing disfavour because of the damaging effects some such toxins may have if released into the aquatic environment under certain circumstances.

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It has been known for many years, for example as disclosed in GB 1,307,001 and US 3,702,778, that certain coatings, for example elastomers such as silicone rubbers, resist fouling by aquatic organisms. Such coatings are non-biocidal, generally hydrophobic and are believed to present a surface which physically deters settlement and/or to which the organisms cannot easily adhere, and they can accordingly be called foul release coatings rather than anti-fouling coatings. Foul release properties can be characterised by barnacle adhesion measurements, for example, ASTM D 5618-94. The following barnacle adhesion values have been recorded by this method: Silicone surface (0.05 MPa), Polypropylene surface (0.85 MPa), Polycarbonate surface (0.96 MPa), Epoxy surface (1.52 MPa) and Urethane surface (1.53 MPa) (J.C. Lewthwaite, A.F. Molland and K. W. Thomas, "An Investigation into the variation of ship skin fictional resistance with fouling", Trans. R.I.N.A., Vol. 127, pp. 269-284, London (1984)). As an indication of whether or not a coating may be considered to be foul-release: a foul-release coating usually has a mean barnacle adhesion value of less than 0.4MPa.

Silicone rubbers and silicone compounds generally have very low toxicity. A disadvantage of this foul release system when applied to boat hulls is that although the accumulation of fouling organisms is reduced, relatively high vessel speeds are needed to remove all fouling species. Thus, in some instances, it has been shown that it is necessary to sail with a speed of at least 10 knots to satisfactorily remove fouling from a hull that has been treated with such a coating. For this reason silicone rubbers have so far gained only limited commercial success.

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It is also long known that the adhesion of silicone foul release coatings to anticorrosive coatings is generally poor unless a suitable tie-coat or link coat is used to ensure adequate adhesion. Such tie coats often contain a silicone. Examples of silicone containing tie coats are described in EP521983 and
5 EP1832630.

The combination of a suitable tie-coat with a second coating layer is sometimes referred to as a 'duplex' foul release system. Hitherto, the compositions described in the prior-art for use as the tie-coat in such duplex systems are
10 generally free of added biocides and WO2008/013825 explicitly teaches away from using biocides as part of their systems.

GB1409048 discloses a marine polyurethane top coat composition capable of imbibing 30 to 300% of its own weight of seawater which is applied over a
15 biocidal antifouling coating. The polyurethane top coat of GB1409048 is not foul release coating within the context of the present invention (see: 'Redefining antifouling coatings', Journal of Protective Coatings and Linings, September 1999, pages 26-35 which discloses that polyurethanes have extremely high barnacle adhesion strengths in comparison to silicones). No subsequent foul
20 release coating layer is disclosed or suggested in GB1409048.

EP 0 313 233 describes an antifouling marine coating comprising a first layer of anti-fouling corrosion-resisting marine paint containing a toxicant to marine organisms and a second layer of porous organic polymeric membrane adhered
25 to said first layer; the porous organic polymeric membrane preferably being polytetrafluoroethylene (EPTFE). A porous organic polymeric membrane is not a coating in the context of the present invention since is not applied as a liquid mixture which then dries or cures to form a dry continuous film. Furthermore, polytetrafluoroethylene is a material that is unsuitable for use as a foul release
30 surface (see: the above-noted 'Redefining antifouling coatings' which indicates

a high barnacle adhesion strength). The use of a subsequent foul release coating layer is neither disclosed nor suggested in EP 0 313 233.

US 4,129,610 describes a water soluble coating composition for ship bottoms comprising a vinyl copolymer and a water-soluble epoxy compound. The water soluble coating composition is applied on a primer coating layer having a toxic material. The water soluble coating composition of US 4,129,610 is not considered a foul release coating within the context of the present invention (see the above-noted 'Redefining antifouling coatings' article which reports the barnacle adhesion strength of epoxy coatings is extremely high). The use of a subsequent foul release coating layer is neither disclosed nor suggested.

FR2636958 describes a chlorinated adhesion primer for a silicone elastomer. According to this publication a triorganotin oxide or halide biocide or copper oxide may be added to the primer. Tributyl tin oxide or fluoride and copper oxide are the only mentioned suitable biocide additives to such a system and there is no example or further description of a primer containing any biocide. The document is completely silent on leaching of biocide and there is no enabling teaching of a foul release system with a primer that contains any biocide.

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WO95/32862 discloses a duplex foul release system which can be used on a substrate for countering fouling by marine organisms. The duplex system consists of a bonding layer and a release layer wherein a 3-isothiazolone biocide is embedded in either the bonding layer or release layer. The document teaches exclusively that 3-isothiazolones should be used as the biocide and that the leaching rate of the biocide from the bonding layer is inversely proportional to the square root of time, and no other factors control the leaching rate other than potentially the solubility of the biocide in water. The leaching of biocide is therefore only poorly controlled in such systems and does not qualify as a biocidal foul release coating system having a controlled leaching rate of the biocide within the framework of the present invention. It was found that

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substrates coated with systems, like the one disclosed in WO 95/32862 where the leaching rate of the biocide from the bonding layer is inversely proportional to the square root of time, shortly after immersion of the substrate in seawater, the substrate remains substantially free of fouling and exhibit superior performance in comparison substrates coated with a biocide-free foul release coating system. However, the superior performance is not sustained, the coated substrates become progressively covered with biofouling, and within 4-6 months the system of WO 95/32862 shows similar severe fouling as substrates coated with a biocide-free foul release coating system.

SUMMARY OF THE INVENTION

Surprisingly it was found that a structure coated with a biocidal foul release coating system can be made that shows a controlled leaching of biocide.

According to the present invention, such structure can be obtained by

- a. providing a substrate,
- b. coating the substrate with a first coating layer,
- c. applying at least one subsequent coating layer on top of the first coating layer,

wherein the first and the subsequent coating layer(s) form a biocidal foul release coating system, the first coating layer contains a biocide, the subsequent coating layer(s) contain(s) less biocide than the first coating layer, and the subsequent coating layer(s) is(are) free or substantially free of biocide.

The biocidal foul release coating systems as defined in the present application shows a controlled leaching of the biocide.

By showing a controlled leaching of the biocide we mean that the ratio of the release rate of biocide from the foul release coating system of this invention, 5 days after application of the coating (R_5) and the release rate of biocide 30 days

after application of the coating (R_{30}) R_5/R_{30} is less than or equal to ($\leq$) 1.5, preferably ≤ 1.33 , more preferably ≤ 1.11 .

5 The biocidal foul release coating systems of the present invention show excellent fouling resistance both at short time and longer time after immersion of the substrates in seawater.

Within the framework of the present invention, a biocidal foul release coating system is a coating system having a surface which physically deters settlement
10 and/or to which aquatic/marine organisms cannot easily adhere and where biocide is released from the coating system.

To improve the adhesion of the first coating layer to the substrate, there might be a tie-coat or adhesion promoter layer between the substrate and the first
15 coating layer. To improve the corrosion resistance of the substrate, there might also be an anticorrosive coating applied on the substrate before the first coating layer is applied. More in general, there might be one or more coating layer(s) on the substrate before the first coating layer, comprising the biocide, is applied to the substrate.

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To prepare a coating layer, a coating composition is applied to the surface (e.g. to the substrate or another coating layer) as a liquid mixture; the coating composition then dries or cures to form a dry continuous coating film/layer over that surface.

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The present inventors have realised that the rate of biocide leaching from the biocidal foul release coating system can be controlled by applying a subsequent coating layer or layers on top of a first coating layer, wherein the first coating layer contains a biocide, the subsequent coating layer(s) containing less biocide
30 than the first coating layer and being free or substantially free of biocide. The advantage of this is that the biocide leaching rate can be tuned, made less

dependent on time and indeed maintained in a more linear relationship with time. Therefore a desired and more constant rate of biocide leaching can be attained. This is advantageous as it leads to extended performance lifetimes, more efficient use of the biocide, and reduced environmental impact.

5 Furthermore, biocide leaching can be controlled such that the ability of the fouling release coating system to prevent fouling under low speed or static conditions is especially enhanced.

In the context of the present invention biocide leaching (sometimes known as

10 biocide release) and biocide leaching rate (biocide release rate) should be clearly differentiated from foul release. Leaching rate is the rate at which the biocide is released by the coating system into the surrounding waters and is typically expressed as mass of biocide per unit area per unit time. Foul release is concerned with prevention of fouling and/or its ease of removal from the

15 surface of an immersed substrate by non-biocidal means. For example foul release properties can be characterised by barnacle adhesion measurements that can be carried out using ASTM D 5618-94, Standard test method for measurement of barnacle adhesion strength in shear, or a related method. Both are complementary mechanisms to control fouling but are independent of each

20 other.

More particularly, the present inventors have realised that the leaching rate can be controlled by varying the composition of the subsequent coating layer(s). The first coating layer behaves as a reservoir of biocide which contains a ready

25 supply of biocide to be released. The leaching rate of the biocide can be controlled by varying certain attributes of the first and subsequent coating layer(s). These attributes include, but are not limited to: pigment volume concentration, cross link density, pigment size and shape, molecular weight of the polymer, the presence and amount of an incompatible fluid, the cross linking

30 chemistry of the subsequent coating layer(s) and film thickness.

The reservoir of biocide, combined with the control mechanism of the subsequent coating layer(s), allows the biocide leaching rate to be tailored to the end use.

- 5 Within the framework of the present invention a coating systems that shows a controlled leaching of biocide is a system where the release rate of biocide 30 days after immersion in water (R_{30}) is at least 67% of the release rate 5 days after immersion in water (R_5). In other words, a coating systems showing a controlled leaching of biocide is a system where $R_5/R_{30} \leq 1.5$.

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In one embodiment of the present invention, $R_5/R_{30} \leq 1.5$. In a further embodiment of the present invention, $R_5/R_{30} \leq 1.33$. In an even further embodiment of the present invention $R_5/R_{30} \leq 1.11$.

- 15 In WO95/32862 the duplex foul release system is described as having a leaching rate of the biocide from the bonding layer that is inversely proportional to the square root of time, and no other factors control the leaching rate other than potentially the solubility of the biocide in water. For this system, the release rate of the biocide is described as $F(t) \sim 36/t^{0.5}$, where F is the leach rate in $\mu\text{g}/\text{cm}^2/\text{day}$ ($\mu\text{g cm}^{-2} \text{ day}^{-1}$) and t is the time in days. For this system, $R_5/R_{30} = F(5)/F(30) = 30^{0.5}/5^{0.5} = 2.45$. WO95/32862 fails to teach that a biocidal foul release coating system, wherein the substrate is first coated with a coating layer containing a biocide, which is then over-coated with subsequent layer(s) containing substantially no biocide would result in a more gradual and sustained
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- 25 release profile of biocide from the foul release coating surface.

- According to the present invention, the subsequent coating layer(s) that are applied on top of the first coating layer contains less biocide than the first coating layer. Further, the subsequent coating layer(s) is(are) free or
- 30 substantially free of biocide. Substantially free of biocide means that the subsequent coating layer(s) contains less than 1.0 wt% (based on the total

weight of the coating composition) of biocide. Preferably the subsequent coating layer(s) contain less than 0.5 wt% of biocide, more preferably less than 0.1 wt%. For the avoidance of doubt, weight percent (wt %) is the weight percent, based on the total weight of the coating composition.

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In one embodiment the subsequent coating layer(s) further comprises an incompatible fluid.

10 The incompatible fluid in the subsequent coating layer(s) helps to achieve an improved foul release performance. Without wishing to be bound by theory it is believed that the fluid may have an effect upon transportation of the biocide.

In a further embodiment the biocide is either partially or wholly encapsulated or adsorbed or supported or bound.

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Encapsulation or absorption or supporting or binding of the biocide can provide a secondary mechanism for controlling biocide leaching from the coating system in order to achieve an even more gradual release and long lasting effect.

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The present invention relates to (i) a biocidal foul release coating system, and to (ii) a structure coated with the biocidal foul release coating system, the biocidal foul release coating system comprising

- a. a substrate,
 - 25 b. a first coating layer,
 - c. at least one subsequent coating layer on top of the first coating layer, the first coating layer containing a biocide, the subsequent coating layer(s) containing less biocide than the first coating layer, and the subsequent coating layer(s) being free or substantially free of biocide. The biocidal foul release
- 30 coating system shows a controlled leaching of the biocide.

One embodiment of the present invention is a structure coated with the biocidal foul release coating system defined above.

DETAILED DESCRIPTION

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First coating layer containing a biocide

The composition of the first coating layer is not especially limiting but preferably the first coating layer composition comprises a polymer. The polymer preferably forms an elastomer. More preferably this is a polyorganosiloxane. Even more preferably this is a polydimethylsiloxane. Furthermore, the polyorganosiloxane may also comprise two or more polyorganosiloxanes of different viscosity.

Preferably the polyorganosiloxane has one or more, more preferably two or more reactive functional groups such as hydroxyl, alkoxy, acetoxy, carboxyl, hydrosilyl, amine, epoxy, vinyl or oxime functional groups.

Preferably the polymer is present in an amount of 5 to 50wt% based on the total weight of the coating composition. More preferably this is present in an amount of 8 to 20wt%.

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Preferably the polymer is crosslinkable. Depending on the type of crosslinkable polymer, the coating composition may require a cross-linker. The necessity for the presence of cross-linker will depend on the type and number of functional groups that are present in said polymer. If the polymer comprises alkoxy-silyl groups, the presence of a small amount of water, and optionally, a condensation catalyst is generally sufficient to achieve full cure of the coating after application. For these compositions, atmospheric moisture is generally sufficient to induce curing, and as a rule it will not be necessary to heat the coating composition after application.

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The optionally present cross-linker can be a cross-linking agent comprising a functional silane and/or one or more of any of acetoxo, alkoxy, amido, alkenoxy and oxime groups. Examples of such cross-linking agents are presented in WO 99/33927, page 19, line 9, through page 21, line 17. Mixtures of different cross-linkers can also be used.

Preferably the crosslinking agent is present in an amount of 0.1% to 20wt% based on the total weight of the coating composition.

10 The first coating layer contains a biocide. By "contains"/"containing", we mean that the biocide is present within the body of the coating layer (in the sense that it was mixed in the coating composition prior to curing/drying).

The biocide of the present invention can be one or more of an inorganic, organometallic, metal-organic or organic biocide for marine or freshwater organisms. Examples of inorganic biocides include copper salts such as copper oxide, copper thiocyanate, copper bronze, copper carbonate, copper chloride, copper nickel alloys, and silver salts such as silver chloride or nitrate; organometallic and metal-organic biocides include zinc pyrithione (the zinc salt of 2-pyridinethiol-1-oxide), copper pyrithione, bis (N-cyclohexyl-diazenium dioxy) copper, zinc ethylene-bis(dithiocarbamate) (i.e. zineb), zinc dimethyl dithiocarbamate (ziram), and manganese ethylene-bis(dithiocarbamate) complexed with zinc salt (i.e. mancozeb); and organic biocides include formaldehyde, dodecylguanidine monohydrochloride, thiabendazole, N-trihalomethyl thiophthalimides, trihalomethyl thiosulphamides, N-aryl maleimides such as N-(2,4,6-trichlorophenyl) maleimide, 3-(3,4-dichlorophenyl)-1,1-dimethylurea (diuron), 2,3,5,6-tetrachloro-4-(methylsulphonyl) pyridine, 2-methylthio-4-butylamino-6-cyclopopylamino-s-triazine, 3-benzo[b]thien-yl-5,6-dihydro-1,4,2-oxathiazine 4-oxide, 4,5-dichloro-2-(n-octyl)-3(2H)-isothiazolone, 2,4,5,6-tetrachloroisophthalonitrile, tolylfluanid, dichlofluanid, diiodomethyl-p-tosylsulphone, capsciadin, N-cyclopropyl-N'-(1,1-dimethylethyl)-6-(methylthio)-

1,3,5-triazine-2,4-diamine, 3-iodo-2-propynylbutyl carbamate, medetomidine, 1,4-dithiaanthraquinone-2,3-dicarbonitrile (dithianon), boranes such as pyridine triphenylborane, a 2-trihalogenomethyl-3-halogeno-4-cyano pyrrole derivative substituted in position 5 and optionally in position 1, such as 2-(p-chlorophenyl)-
5 3-cyano-4-bromo-5-trifluoromethyl pyrrole (tralopyril), and a furanone, such as 3-butyl-5-(dibromomethylidene)-2(5H)-furanone, and mixtures thereof, macrocyclic lactones such as avermectins, for example avermectin B1, ivermectin, doramectin, abamectin, amamectin and selamectin, and quaternary ammonium salts such as didecyldimethylammonium chloride and an
10 alkyl dimethylbenzylammonium chloride. In one embodiment, the biocide may be a 3-isothiazolone, however the inventors have found that this biocide should preferably be in an encapsulated, adsorbed or bound form. In another embodiment, the biocide is not a 3-isothiazolone.

15 Preferably the biocide is organic or metal-organic. Without wishing to be bound by theory, it is believed that leaching of the biocide involves physical diffusion of the biocide from the first coating layer through the subsequent coating layer(s) by passive transport processes. The flux of biocide from the coating system will therefore be controlled in part by the diffusion of the biocide through, and
20 compatibility with, the subsequent coating layer(s). If the diffusion or compatibility are inherently high, as would be anticipated for organometallic biocides such as organotin and the like, then the resulting leaching rate will also be inherently high and difficult to control, such that the lifetime of the coating will be reduced and undesirable environmental impact may result. If the
25 diffusion or compatibility are inherently low, as would be anticipated for inorganic biocides such as the inorganic salts of copper and the like, then the leaching rate will also be inherently low and fouling may result. In general, the use of an organic or metal-organic biocide allows the leaching rate to be suitably controlled through use of the coating system of the present invention
30 and unacceptable environmental damage to be avoided.

In the context of the present invention, an inorganic biocide is a biocide whose chemical structure comprises a metal atom and which is free of carbon atoms; an organometallic biocide is a biocide whose chemical structure comprises a metal atom, a carbon atom, and a metal-carbon bond; a metal-organic biocide
5 is a biocide whose chemical structure comprises a metal atom, a carbon atom, and which is free of metal-carbon bonds; and an organic biocide is biocide whose chemical structure comprises a carbon atom and which is free of metal atoms.

10 Preferably, for excellent antifouling properties the biocide is one or more of a 2-trihalogenomethyl-3-halogeno-4-cyano pyrrole derivative substituted in position 5 and optionally in position 1, such as tralopyril, 1,4-dithiaanthraquinone-2,3-dicarbonitrile (dithianon), copper pyrithione, zinc pyrithione, tolylfluanid, dichlofluanid, and N-cyclopropyl-N'-(1,1-dimethylethyl)-6-(methylthio)-1,3,5-
15 triazine-2,4-diamine.

Preferably the biocide(s) is(are) present in the first coating layer composition in an amount of 0.05 to 50wt %, more preferably 3 to 30wt%, and most preferably 10 to 20wt% based on the total weight of the composition of the first coating
20 layer. In any case, the amount of biocide present in the first coating layer, must be more than the amount of biocide in the at least one subsequent coating layer(s) at the time the coating layers are applied to the substrate.

Furthermore, the biocide may optionally be wholly or partially encapsulated, adsorbed or supported or bound. Certain biocides are difficult or hazardous to
25 handle and are advantageously used in an encapsulated or absorbed or supported or bound form. Additionally, encapsulation, absorption or support or binding of the biocide can provide a secondary mechanism for controlling biocide leaching rate from the coating system in order to achieve an even more
30 gradual release and long lasting effect.

The method of encapsulation, adsorption or support or binding of the biocide is not particularly limiting for the present invention. Examples of ways in which an encapsulated biocide may be prepared for use in the present invention include mono and dual walled amino-formaldehyde or hydrolysed polyvinyl acetate-phenolic resin capsules or microcapsules as described in EP1791424. An example of a suitable encapsulated biocide is encapsulated 4,5-dichloro-2-(n-octyl)-3(2H)-isothiazolone marketed as by Dow Microbial Control as Sea-Nine CR2 Marine Antifoulant Agent.

Examples of ways in which an absorbed or supported or bound biocide may be prepared include the use of host-guest complexes such as clathrates as described in EP0709358, phenolic resins as described in EP0880892, carbon-based adsorbents such as those described in EP1142477, or inorganic microporous carriers such as the amorphous silicas, amorphous aluminas, pseudoboehmites or zeolites described in EP1115282.

Where the polymer of the biocidal first coating layer composition is crosslinkable, the composition may optionally comprise a catalyst. Examples of suitable catalysts are the carboxylic acid salts of various metals, such as tin, zinc, iron, lead, barium, and zirconium. The salts preferably are salts of long-chain carboxylic acids, for example dibutyltin dilaurate, dibutyltin dioctoate, iron stearate, tin (II) octoate, and lead octoate. Further examples of suitable catalysts include organobismuth and organotitanium compounds and organophosphates such as bis(2-ethyl-hexyl) hydrogen phosphate. Other possible catalysts include chelates, for example dibutyltin acetoacetate. Further, the catalyst may comprise a halogenated organic acid which has at least one halogen substituent on a carbon atom which is in the [alpha]-position relative to the acid group and/or at least one halogen substituent on a carbon atom which is in the [beta]-position relative to the acid group, or a derivative which is hydrolysable to form such an acid under the conditions of the condensation reaction.

Alternatively, the catalyst may be as described in any of WO2007122325A1, WO2008055985A1, WO2009106717A2, WO2009106718A2, WO2009106719A1, WO2009106720A1, WO2009106721A1, 5 WO2009106722A1, WO2009106723A1, WO2009106724A1, WO2009103894A1, WO2009118307A1, WO2009133084A1, WO2009133085A1, WO2009156608A2, and WO2009156609A2.

10 The catalyst of the biocidal first coating layer composition is preferably present in an amount of 0.01 to 4 wt%, based on the total weight of the coating composition.

Preferably, the biocidal first coating layer composition according to the invention also comprises one or more fillers, pigments, additional catalysts, and/or 15 solvents. Examples of suitable fillers are barium sulphate, calcium sulphate, calcium carbonate, silicas or silicates (such as talc, feldspar, and china clay), aluminium paste/flakes, bentonite or other clays. Some fillers such as fumed silica may have a thixotropic effect on the coating composition. The proportion of fillers may be in the range of from 0 to 25wt%, based on the total weight of 20 the coating composition. Preferably the clay is present in an amount of from 0 to 1wt% and preferably the thixotrope is present in an amount of from 0 to 5wt%, based on the total weight of the coating composition.

Examples of suitable pigments are black iron oxide, red iron oxide, yellow iron 25 oxide, titanium dioxide, zinc oxide, carbon black, graphite, red molybdate, bismuth vanadate yellow, yellow molybdate, zinc sulfide, antimony oxide, cobalt/zinc titanium oxide greens, zinc/tin titanate oranges, lanthanide sulphide oranges and reds, manganese pyrophosphate violets, sodium aluminium sulfosilicates, quinacridones, phthalocyanine blue, phthalocyanine green, black 30 iron oxide, indanthrone blue, cobalt aluminium oxide, carbazodioxazine, chromium (III) oxide, isoindoline orange, bis-acetoaceto-tolidiole,

benzimidazolone, quinaphthalone yellow, isoindoline yellow, tetrachloroisindolinone, and quinophthalone yellow. The proportion of pigments may be in the range of from 0 to 10wt%, based on the total weight of the coating composition. Suitable solvents include aromatic hydrocarbons, alcohols, ketones, esters, and mixtures of the above with one another or an aliphatic hydrocarbon. Preferable solvents include methyl isoamylketone and/or xylene. Preferably the solvent is present in an amount of 10 to 40wt% based on the total weight of the composition.

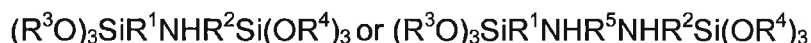
- 10 The composition optionally includes an adhesion promoting material, typically in an amount of 0.01-0.5wt% based on the total weight of the composition. Examples of suitable adhesion promoters include silanes such as aminosilanes, epoxysilanes, methacryoxyloxypropylsilanes and mercaptosilanes.

Preferably the adhesion promoter is an aminosilane of the type:



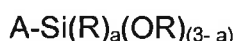
- wherein each R independently is selected from C1-8 alkyl (e.g. methyl, ethyl, hexyl, octyl, etc.), C1-4 alkyl, O, C2-4 alkyl; aryl (e.g. phenyl) and aryl C1-4 alkyl (e.g. benzyl); R¹ is selected from (CH₂)₁₋₄, methyl-substituted trimethylene and (CH₂)₂₋₃, O, (CH₂)₂₋₃; R² is selected from hydrogen, an alkyl, cycloalkyl, arakyl or aryl group or (CH₂)₂₋₄-NH₂.

Alternatively, the adhesion promoter is a "dipodal" silane as mentioned in WO2010018164 of the type



- 25 where R¹, R² and R⁵ independently are C1 to C5 alkylene groups and R³ and R⁴ independently are selected from methyl or ethyl.

Alternatively, the adhesion promoter is an epoxysilane of the type:



- 30 where A is an epoxide substituted monovalent hydrocarbon radical having 2 to 12 carbon atoms; and each R independently is selected from C1-8 alkyl (e.g.

methyl, ethyl, hexyl, octyl, etc.), C1-4-alkyl-, O-, C2-4-alkyl; aryl (e.g. phenyl) and aryl C1-4 alkyl (e.g. benzyl); and a is 0 or 1.

The group A in the epoxysilane is preferably a glycidoxy-substituted alkyl group, for example 3-glycidoxypropyl. The epoxysilane can for example be 3-
5 glycidoxypropyltrimethoxysilane, 3-glycidoxypropyltriethoxysilane, 3-glycidoxypropyldiethoxymethoxysilane, 2-glycidoxypropyltrimethoxysilane, 2-(3,4-epoxy-4-methylcyclohexyl)-ethyltrimethoxysilane, 5,6-epoxy-hexyltriethoxysilane ; or their oligomers.

- 10 More preferably the adhesion promoter is N-2-aminoethyl-3-aminopropyltrimethoxysilane. Additional optional additives include dispersants such as an unsaturated polyamide acid ester salt.

Subsequent coating layer(s), foul-release layer

- 15 The composition of the subsequent coating layer(s) is not especially limiting but the composition preferably comprises a polymer. Preferably the polymer forms an elastomer. More preferably this is a polyorganosiloxane. Even more preferably this is a polydimethylsiloxane. Furthermore, the polyorganosiloxane may also comprise two or more polyorganosiloxanes of different viscosity.

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The polyorganosiloxane has one or more, preferably two or more reactive functional groups such as hydroxyl, alkoxy, acetoxy, carboxyl, hydrosilyl, amine, epoxy, vinyl or oxime functional groups.

- 25 Alternatively, the polymer may be as described in WO2008132196, wherein the polymer is a polyorganosiloxane polyoxyalkylene block copolymer of the form PS – (A – PO – A – PS)_n, wherein PS represents a polyorganosiloxane block, PO represents a polyoxyalkylene block, A represents a divalent moiety, and n has a value of 1 or more than 1.

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The polymer has two or three reactive groups X on a polyorganosiloxane block per molecule which may self-condense and crosslink in the presence or absence of a catalyst (as defined earlier in this document) which can, optionally, be crosslinked with another organosilicon crosslinking agent containing two or more groups Y which are reactive with the said groups X.

Preferably the polyorganosiloxane(s) polymer(s) is(are) present in an amount of 30 to 90 wt%, based on the total weight of the coating composition.

Preferably the polymer is crosslinkable. Depending on the type of crosslinkable polymer, the coating composition may require a cross-linker. The presence of a cross-linker is only necessary if the curable polymer cannot be cured by condensation. This will depend on the type and number of functional groups that are present in said polymer. If the polymer comprises alkoxy-silyl groups, the presence of a small amount of water, and optionally a condensation catalyst is generally sufficient to achieve full cure of the coating after application. For these compositions, atmospheric moisture is generally sufficient to induce curing, and as a rule it will not be necessary to heat the coating composition after application.

20

The optionally present cross-linker can be a cross-linking agent comprising a functional silane and/or one or more of any of acetoxo, alkoxy, amido, alkenoxy and oxime groups. Examples of such cross-linking agents are presented in WO 99/33927, page 19, line 9, through page 21, line 17. Mixtures of different cross-linkers can also be used.

Preferably the crosslinking agent is present in an amount of 1 to 25wt% based on the total weight of the coating composition.

Where the polymer of the subsequent coating layer composition is crosslinkable, the composition may optionally comprise a catalyst. Examples of

suitable catalysts are the carboxylic acid salts of various metals, such as tin, zinc, iron, lead, barium, and zirconium. The salts preferably are salts of long-chain carboxylic acids, for example dibutyltin dilaurate, dibutyltin dioctate, iron stearate, tin (II) octoate, and lead octoate. Further examples of suitable catalysts include organobismuth and organotitanium compounds and organophosphates such as bis(2-ethyl-hexyl) hydrogen phosphate. Other possible catalysts include chelates, for example dibutyltin acetoacetate. Further, the catalyst may comprise a halogenated organic acid which has at least one halogen substituent on a carbon atom which is in the [alpha]-position relative to the acid group and/or at least one halogen substituent on a carbon atom which is in the [beta]-position relative to the acid group, or a derivative which is hydrolysable to form such an acid under the conditions of a condensation reaction.

Alternatively, the catalyst may be as described in any of WO2007122325A1, WO2008055985A1, WO2009106717A2, WO2009106718A2, WO2009106719A1, WO2009106720A1, WO2009106721A1, WO2009106722A1, WO2009106723A1, WO2009106724A1, WO2009103894A1, WO2009118307A1, WO2009133084A1, WO2009133085A1, WO2009156608A2, and WO2009156609A2.

Preferably the catalyst is present in an amount of 0.05 to 4wt% based on the total weight of the coating composition.

Preferably, the subsequent coating layer composition according to the invention also comprises one or more fillers, pigments, catalysts, and/or solvents. Examples of suitable fillers are barium sulphate, calcium sulphate, calcium carbonate, silicas or silicates (such as talc, feldspar, and china clay), aluminium paste/flakes, bentonite or other clays. Some fillers such as fumed silica may have a thixotropic effect on the coating composition. The proportion of fillers may be in the range of from 0 to 25 wt%, based on the total weight of the coating composition. Preferably the clay is present in an amount of from 0

to 1 wt% and preferably the thixotrope is present in an amount of from 0 to 5 wt%, based on the total weight of the coating composition.

Examples of suitable pigments are black iron oxide, red iron oxide, yellow iron oxide, titanium dioxide, zinc oxide, carbon black, graphite, red molybdate, yellow molybdate, zinc sulfide, antimony oxide, sodium aluminium sulfosilicates, quinacridones, phthalocyanine blue, phthalocyanine green, black iron oxide, indanthrone blue, cobalt aluminium oxide, carbazodioxazine, chromium oxide, isoindoline orange, bis-acetoaceto-tolidiole, benzimidazolone, quinaphthalone yellow, isoindoline yellow, tetrachloroisoindolinone, and quinophthalone yellow. The proportion of pigments may be in the range of from 0 to 25 wt%, based on the total weight of the coating composition. Suitable solvents include aromatic hydrocarbons, alcohols, ketones, esters, and mixtures of the above with one another or an aliphatic hydrocarbon. Preferable solvents include methyl isoamyl ketone and/or xylene. Preferably the solvent is present in an amount of 0-40wt%, based on the total weight of the composition.

The foul release properties of the coating system of the present invention are generally improved when the subsequent coating layer(s) composition forms a generally hydrophobic or amphiphilic foul release coat when dried or cured. The bulk and surface hydrophobicity of the subsequent coating layer(s) can be characterised by various means, for example, by seawater uptake measurements or surface contact angle measurements. Preferably, the seawater uptake of the subsequent coating layer(s) is less than 30% by mass, more preferably less than 25% by mass. Preferably the equilibrium water contact angle of the subsequent coating layer(s) is greater than 30 degrees at 23 °C.

In a preferred embodiment the subsequent coating layer(s) composition comprises an incompatible fluid or grease. In the context of the present invention an incompatible fluid means a silicone, organic or inorganic molecule

or polymer, usually a liquid, but optionally also an organosoluble grease or wax, which is immiscible (either wholly or partly) with (the elastomer network of) the subsequent coating layer(s). Once the first coating layer and subsequent coating layers have cured, the fluid will form become enriched at the surface of the subsequent coating layer(s) and augment its foul release properties. An example of an incompatible fluid is provided in WO2007/10274. In WO2007/10274, the incompatible fluid is a fluorinated polymer or oligomer in a polysiloxane coating; the process of enrichment of the fluorinated polymer/oligomer at the surface of the cured polysiloxane coating layer is thermodynamically driven due to the difference in surface energy. The low surface energy provided by the fluorinated polymer or oligomer in combination with the elastic properties provided by the cured polysiloxane improves the fouling release properties of the coating.

Examples of suitable fluids are:

- a) Linear and trifluoromethyl branched fluorine end-capped perfluoropolyethers (eg Fomblin Y®, Krytox K® fluids, or Demnum S® oils);
- b) Linear di-organo (OH) end-capped perfluoropolyethers (eg Fomblin Z DOL®, Fluorolink E®);
- c) Low MW polychlorotrifluoroethylenes (eg Daifloil CTFE® fluids)

In all cases the fluorinated alkyl- or alkoxy containing polymer or oligomer does not substantially take part in any cross-linking reaction. Other mono- and diorgano-functional end-capped fluorinated alkyl- or alkoxy- containing polymers or oligomers can also be used (eg carboxy-, ester- functional fluorinated alkyl- or alkoxy-containing polymers or oligomers).

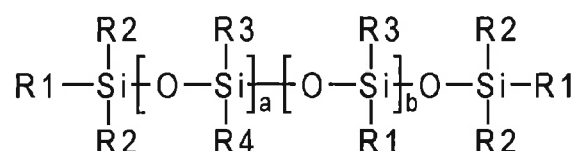
Alternatively, the fluid can be a silicone oil, for example of the formula:



wherein each group Q represents a hydrocarbon radical having 1-10 carbon atoms and n is an integer such that the silicone oil has a viscosity of 20 to 5000

m Pa s. At least 10% of the groups Q are generally methyl groups and at least 2% of the groups Q are phenyl groups. Most preferably, at least 10% of the –SiQ₂-O- units are methyl-phenylsiloxane units. Most preferably the silicone oil is a methyl terminated poly(methylphenylsiloxane). The oil preferably has a viscosity of 20 to 1000 m Pa s. Examples of suitable silicone oils are sold under the trademarks Rhodorsil Huile 510V100 and Rhodorsil Huile 550 by Bluestar Silicones. The silicone oil improves the resistance of the coating system to aquatic fouling.

10 The fluid may also be an organosilicone as shown:



wherein:

- 15 - R1 may be the same or different and is selected from alkyl, aryl, and alkenyl groups, optionally substituted with an amine group, an oxygen-containing group of the formula OR₅, wherein R₅ is hydrogen or a C1-6 alkyl, and a functional group according the formula (I):



wherein:

- R6 is selected from alkyl, hydroxyalkyl, carboxyalkyl of 1 to 12 carbon atoms, and polyoxyalkylene of up to 10 carbon atoms;
- 25 - R7 is selected from hydrogen, alkyl, hydroxyalkyl, carboxyalkyl of 1 to 6 carbon atoms, and polyoxyalkylene of 1 to 10 carbon atoms; R7 may be bonded to R8 to form a ring;
- R8 is an alkyl group with 1-20 carbon atoms;

- R9 is hydrogen or an alkyl group with 1-10 carbon atoms, optionally substituted with oxygen- or nitrogen-containing groups;
- X is selected from O, S and NH;
- provided that at least one R1-group in the organosilicone polymer is a functional group according to the above formula (I) or a salt derivative thereof;
- R2 may be the same or different and is selected from alkyl, aryl, and alkenyl;
- R3 and R4, which may be the same or different, are selected from alkyl, aryl, capped or uncapped polyoxyalkylene, alkaryl, aralkylene, and alkenyl;
- a is an integer from 0 to 50,000;
- b is an integer from 0 to 100; and
- a+b is at least 25.

In one embodiment

- R2, R3 and R4 are independently selected from methyl and phenyl, more preferably methyl.
- R6 is an alkyl group with 1-12, more preferably 2-5 carbon atoms.
- R7 is hydrogen or an alkyl group with 1-4 carbon atoms.
- R8 is an alkyl group with 2-10 carbon atoms.
- R9 is hydrogen or an alkyl group with 1-5 carbon atoms.
- X is an oxygen atom.
- a+b ranges from 100 to 300.

In one embodiment the fluid is present in 0.01 to 10wt%, based on the total weight of the coating composition. Most preferably the fluid is present in the range of 2 to 7wt%.

Method of controlling the rate of release of biocide

According to the present invention, there is provided a method of controlling the rate of release of biocide from a foul release coating system wherein the ratio of the release rate of biocide from a foul release coating system wherein the ratio of
5 the release rate of biocide from the foul release coating system 5 days after application of the coating (R_5) and the release rate of biocide 30 days after application of the coating (R_{30}) $R_5/R_{30} \leq 1.5$, the method comprising

- 10 a. providing a substrate,
 b. coating the substrate with a first coating layer,
 c. applying at least one subsequent coating layer on top of the first coating layer,
- 15 the first coating layer containing a biocide, the subsequent coating layer(s) containing less biocide than the first coating layer and being free or substantially free of biocide.

In one embodiment, the method of the invention is capable of controlling the rate of release of biocide from a foul release coating system such that the ratio
20 R_5/R_{30} is less than or equal to ($\leq$) 1.33, and preferably less than or equal to ($\leq$) 1.11.

Suitably, the first coating layer and/or the subsequent coating layer(s)
25 comprises an elastomeric polymer. The elastomeric polymer is as described in all preceding paragraphs.

Suitably, the first coating layer and/or the subsequent coating layer(s) comprise a polyorganosiloxane. The subsequent coating layer(s) are as described in all
30 preceding paragraphs.

Suitably, the substrate is coated with an anticorrosion coating and the first coating layer is used as a tie coat over said anticorrosion coating.

Suitably, the biocide in the first coating layer is an organic or metal-organic biocide. The biocide is as described in all preceding paragraphs.

- 5 Suitably, the biocide is one or more of any of the biocides previously mentioned, and most suitably a 2-trihalomethyl-3-halogeno-4-cyano pyrrole derivative substituted in position 5 and optionally in position 1 or 1,4-dithiaanthraquinone-2,3-dicarbonitrile.
- 10 Suitably, the subsequent coating layer(s) comprises an incompatible fluid such as a silicone, organic or inorganic molecule or polymer, which is immiscible with the subsequent coating layer(s).

Application

- 15 The coating system according to the present invention can be applied to a substrate by normal techniques, such as brushing, roller coating, dipping or spraying (airless and conventional).

After the subsequent coating layer(s) has cured, it can be immersed
20 immediately and gives immediate anti-fouling and fouling-release protection. The resulting coating system has very good anti-fouling and fouling-release properties. This makes the coating system according to the present invention very suitable for use in preventing fouling in marine and freshwater applications. The coating system can be used for both dynamic and static structures, such as
25 ship and boat hulls, buoys, drilling platforms, oil rigs, floating production storage and offloading vessels (FPSOs), pipes, cooling water intakes in power plants, fish nets, fish cages and other aquaculture and marine apparatus/structures and the like which are wholly or partially immersed in water. The coating system can be applied on any substrate that is used for these structures, such as metal e.g.
30 steel, aluminium, concrete, wood, plastic or fibre-reinforced resin.

In addition to the coating system according to the present invention having a controlled rate of release of biocide from a foul release coating system such that the ratio of the release rate of biocide from the foul release coating system 5 days after application of the coating (R_5) and the release rate of biocide 30 days after application of the coating (R_{30}) R_5/R_{30} is less than or equal to ($\leq$) 1.5 (preferably ≤ 1.33), it has also been found to be effective against a broader range of fouling-types including (i) slime fouling, (ii) weed fouling, (iii) soft bodied fouling and (iv) hard bodied fouling, particularly on slow moving aquatic vessels, compared to systems which do not comprise a biocide or a foul-release coating layer.

The coating system may be applied directly to a non-treated substrate. Alternatively, the coating system of the present invention may be applied to a substrate to which surface treatments or other coating layers have been previously applied. Examples of such surface treatments and other coating layers include anticorrosion coatings, biocidal antifouling coatings, sealer coats, tie-coats, adhesion promoting layers, and the like.

For application to ship and boat hulls at newbuilding, the system would typically be applied directly over a substrate having one or more anticorrosive coatings. At maintenance and repair or recoat, the scheme would typically be applied optionally over the existing coating scheme (with optional link coat) or directly over the substrate after removal of the existing coating scheme and reapplication of one or more anticorrosive coatings.

The substrate for which fouling is to be inhibited is not especially limited and includes any of steel, plastic, concrete, wood, fibre-reinforced resin and aluminium.

In a typical situation, for application on ships and boat hulls, the first coating layer would be applied to result in a dry film thickness in the range of 100 – 200

µm, and the subsequent coating layer(s) would be applied to result in a dry film thickness in the range of 100 – 200 µm. Where a greater dry film thickness is required, the required film thickness may be produced by successive applications, each with a dry film thickness of 100 – 200 µm. On other
5 substrates, the first coating layer would be applied to result in a dry film thickness in the range of 50 – 500 µm, and the subsequent coating layer(s) would be applied to result in a dry film thickness in the range of 50 – 500 µm.

The invention will now be elucidated with reference to the following examples.

10 These are intended to illustrate the invention but are not to be construed as limiting in any manner the scope thereof.

EXAMPLES

15 Examples 1 to 8

Eight different coating systems according to the present invention (Examples 1-8) were prepared.

20 The biocide leaching rate for each coating system was experimentally determined. In summary, duplicate panels coated with each coating system were immersed in a holding tank of synthetic seawater. The panels were periodically transferred to a leaching rate measuring container of fresh synthetic seawater and gently agitated for a fixed period. At the end of this period, the
25 panels were returned to the holding tank and the amount of biocide that had leached into the container was determined by chemical analysis. From knowledge of the determined amount of leached biocide, the exposed surface area of the coated panel, and the period of immersion in the leaching rate measuring container, the biocide leaching rate can be determined and
30 expressed as $\mu\text{g cm}^{-2} \text{ d}^{-1}$.

Artificial seawater

Commercial Instant Ocean Sea Salt was used to prepare artificial seawater by mixing 33g of salt per litre of deionised water.

5 Panel preparation

15 x 10 cm polycarbonate panels were masked to give a known surface area (typically about 100 cm²). 125 µm dry film thickness of a 2 pack epoxy anticorrosive paint (Intershield 300, International Paint) was applied via draw down bar, followed by application of the biocide containing coating layer via draw down bar at 100 µm dry film thickness. Following drying the final 'finish' coat was applied to the film via draw down bar at 15 µm dry film thickness (excluding example 5 where 100 µm dry film thickness was used). The masking tape was removed and the edges of the coated panels were sealed, using a brush, with a 2-pack epoxy anticorrosive paint (Intershield 300, International Paint). Each coat was allowed to cure under ambient conditions before application of a subsequent coating layer(s) and before immersion in the holding tank.

Holding tank

20 The panels were fully immersed in 40 litres of artificial seawater in a rigorously clean glass tank and the water was constantly circulated through an activated carbon filter to avoid build up of the biocide or its degradation products. The temperature of the holding tank was maintained at around 22-23 °C. All panels remained immersed in the holding tank for the duration of the experiment, except during leaching rate measurements which took place on predefined measurement days using the leaching rate measuring container.

Leaching rate measuring container

On predetermined measurement days, panels were transferred to individual rigorously clean lidded polypropylene containers (15 x 8 x 8 cm, l x w x h) containing 100 ml of artificial seawater at a temperature of around 22-23 °C.

The containers were gently agitated using an orbital mixer for 2 hours and the panels were then returned to the holding tank.

Leaching rate determination - General

5

The concentration of biocide in the leaching rate measuring container may be determined using standard analytical methods known to one skilled in the art, for example high performance liquid chromatography (HPLC). The concentration of biocide in the leaching rate measuring container can then be used to determine the leaching rate R using the equation below.

10

$$R = \frac{C \times V \times 24}{t \times A} \mu\text{g cm}^{-2} \text{ d}^{-1}$$

Where C is the equivalent concentration of the biocide in the leaching rate measurement container, V is the volume of artificial seawater in the leaching rate measuring container (litres), t is period of immersion of the panel in the leaching rate measuring container (hours), and A is the exposed surface area of the coating system on the panel (cm²).

15

Leaching rate determination of Examples 1-8– tralopyril

20

Approximately 12 ml of artificial seawater from each leaching rate measuring container was transferred to a glass vial at the end of the agitation period. This vial was held at 45°C overnight to ensure quantitative conversion of the leached tralopyril to 3-bromo-5-(4-chlorophenyl)-4-cyano-1H-pyrrole-3-carboxylic acid (BCCPCA).

25

The concentration of BCCPCA in the treated sample was determined by high performance liquid chromatography (HPLC) by direct injection using an Agilent 1100 HPLC system equipped with a Pursuit UPS 2.4 µm C18 column (50 x 3

30

mm) and using a mixture of acetonitrile, water, and orthophosphoric acid at a ratio of 50:49.95:0.05 parts by volume as mobile phase.

A minimum of 6 calibration standards covering the range from 10 to 500 µg
 5 litre⁻¹ were freshly prepared each day by appropriate dilution with artificial
 seawater of a 1000 µg litre⁻¹ stock solution of BCCPCA in tetrahydrofuran.
 Artificial seawater blanks were analysed before and after the standards and
 after each sample set. Check standards were run after every 5 samples to
 check for reproducibility of the analytical method. At every time point, the
 10 analytical method was proven to be reproducible.

The equivalent concentration of tralopyril in the leaching rate measuring
 container at the end of the agitation period is calculated by multiplying the
 determined BCCPCA concentration by the relative molar masses of tralopyril
 15 and BCCPCA, and the leaching rate of tralopyril, R, is then calculated according
 to the following equation:

$$R = \frac{C_{\text{tralopyril}} \times V \times 24}{t \times A} \mu\text{g cm}^{-2} \text{d}^{-1}$$

20 Where $C_{\text{tralopyril}}$ is the equivalent concentration of tralopyril in the leaching rate
 measurement container, V is the volume of artificial seawater in the leaching
 rate measuring container (litres), t is period of immersion of the panel in the
 leaching rate measuring container (hours), and A is the exposed surface area of
 the coating system on the panel (cm²).

25

Table 3 shows the leaching rate results collected on measurement days 5 (R₅)
 and 30 (R₃₀), and R₅/R₃₀. In each case, the results are the mean results of
 duplicate panels for each coating system.

As can be seen, each coating systems demonstrates controlled leaching as defined within the framework of the present invention and none of the coatings shows biocide leaching rate behaviour that corresponds to the biocide leaching rate being proportional to the square root of time. Moreover, by varying particular parameters of the subsequent coating layer, control can be exercised over the the biocide leaching rate behaviour, which can be made to fall, rise or remain essentially constant over time.

Furthermore, different mean rates of biocide leaching can be attained and, by varying particular parameters of the subsequent coating layer, the biocide leaching rate can be controlled such that a higher or lower biocide leaching rate can be obtained at any given point in time.

Table 1: First coating layer formulation – Examples 1-8

Material	% weight
Polydimethyl siloxane	13.8
Surfactant based on salts of long chain unsaturated polyaminoamides and high molecular weight acid esters	0.6
Tralopyril	13.6
Titanium dioxide	6.7
Fumed silica	0.6
Methyl iso-amyl ketone	18.6
Oxime-cured silicone mastic	37.2
Xylene	7.8
Chlorinated Polyolefin	0.8
N-2-aminoethyl-3-aminopropyltrimethoxysilane	0.2
Diocetylindilaurate	0.1

Table 2: formulation details second coating layer . (Ingredients in vol.% based on total volume of the composition)

<u>Ingredient</u>	<u>Example</u>							
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
Short chain Poly Dimethyl siloxane (viscosity of 7.5 stokes)	59.5							
Silicone polyether block copolymer*		78.6						
Poly Dimethyl siloxane (viscosity of 35 strokes)			65.6	59.5	59.5		59.5	59.5
Fumed silica (Hydrophobic)	1.5	1.8		1.5	1.5		1.5	1.5
Red iron oxide		13.2						
Micaceous iron oxide								7.9
Disparlon 6500 amide (commercial product)		2						
Titanium dioxide	6.5			6.5	6.5		6.5	
Carbon black	1.4			1.4	1.4		1.4	
Xylene	18.4		20.5	18.4	18.4		23.6	18.4
Tetra-ethyl ortho silicate	2.7		3	2.7	2.7		2.7	2.7
polymethyl phenylsiloxane oil	5.2		5.7	5.2	5.2			5.2
2,4-Pentanedione	4.3	3.9	4.7	4.3	4.3		4.3	4.3
Diocetyl tin dilaurate	0.5	0.5	0.5	0.5	0.5		0.5	0.5
Intersleek 970 commercial product						100		

5 *Corresponds to Example 12 of WO 2008/132236

Table 3: Leaching rate results – Examples 1-8

Example	Primary Variable(s)	Mean leaching rate ($\mu\text{g cm}^{-2} \text{d}^{-1}$)		R_5/R_{30}
		$R_5^{1)}$	$R_{30}^{2)}$	
1	Cross-link density	8.4	8.4	1.00
2	Subsequent coating layer(s) chemistry	5.6	7.0	0.80
3	Pigmentation presence	9.7	7.3	1.32
4	Pigment hydrophobicity	10.7	8.5	1.25
5	Thickness of subsequent coating layer(s)	9.0	7.0	1.28
6	Fluid type	9.0	11.0	0.81
7	Presence of fluid	9.6	8.4	1.14
8	Pigment morphology	9.3	10.1	0.92

¹⁾: release rate of biocide 5 days after immersion

²⁾: release rate of biocide 30 days after immersion

5

Examples 9 to 12

As shown in Table 4, further coating systems in accordance with the present invention (Examples 9 to 12) were prepared for comparison with a commercial biocide-free foul release coating system (all Examples).

10

Table 4: First coating layer formulations for Examples 9-12:

Material	% weight
Polydimethyl siloxane	12.80
Surfactant based on salts of long chain unsaturated polyaminoamides and high molecular weight acid esters	0.55
Biocide	20.00
Methyl iso-amyl ketone	23.91
Oxime-cured silicone mastic	34.56
Xylene	6.07
Chlorinated Polyolefin	1.88
N-2-aminoethyl-3-aminopropyltrimethoxysilane	0.16
Dibutyltindilaurate	0.03

Example	Biocide
9	Tralopyril
10	Dithianon
11	Copper Pyrithione (CPT)
12	Zinc Pyrithione (ZPT)

Test panels were prepared in order to determine the ability of each coating system to control the leaching of biocide from the first coating layer and inhibit fouling. The coating systems of Examples 9 to 12 were applied to 60 x 60 cm marine plywood panels by roller to give a dry film thicknesses for the first coating layer and subsequent coating layer of about 100 and 150 μm respectively. The boards had been pre-primed with one coat of a 2 pack epoxy anticorrosive paint (Intershield 300, International Paint) with a DFT of about 125 μm per coat. One half of each panel (the left hand side) was coated with a coating system corresponding to one of the Example 9 to 12 coating systems and, as a control, the other half of the panel (right hand side) was coated with a commercial foul release tie-coat (Intersleek 737, International Paint). Both sides then had a standard foul-release finish coat applied (Intersleek 757, International paint). Each coat was allowed to cure fully under ambient conditions before application of a subsequent coating layer(s) and the start of testing.

Test panels were simultaneously immersed in natural tropical marine waters at a depth of 0.5 to 1.0 m in Changi, Singapore where fouling growth is known to be severe. The panels were periodically removed from the water, photographed and the growth of fouling on the coating systems was assessed prior to re-immersion of the panels.

The coating systems containing tralopyril (Example 9) and dithianon (Example 10) remained substantially free of fouling even after immersion for 8 months. The coating systems containing copper pyrithione (Example 11) and zinc pyrithione (Example 12) exhibited more severe fouling growth than Examples

9 and 10 after 8 months than but less severe fouling growth than the control coatings.

In all cases, the coating systems of Examples 9 to 12 were free of blisters,
5 and cracks after 8 months immersion.

These results clearly show that the ability of the coating systems according to
the present invention to inhibit fouling over an extended period is significantly
improved over the standard commercial foul release coating system.

10

CLAIMS

1. Structure coated with a biocidal foul release coating system, the structure being obtained by
 - a. providing a substrate,
 - b. coating the substrate with a first coating layer,
 - c. applying at least one subsequent coating layer on top of the first coating layer,
 the first coating layer formed from a coating composition containing a biocide, the subsequent coating layer(s) formed from coating composition(s) containing less biocide than the coating composition forming the first coating layer and which is(are) free or substantially free of biocide, and wherein the first and the subsequent coating layer(s) form a biocidal foul release coating system, and wherein the first coating layer and/or the subsequent coating layer(s) comprise a polyorganosiloxane and fumed silica .
2. Structure according to claim 1, showing a controlled leaching of the biocide wherein the ratio of the release rate of biocide from the foul release coating system 5 days after application of the coating (R_5) and the release rate of biocide 30 days after application of the coating (R_{30}) $R_5/R_{30} \leq 1.5$.
3. Structure according to claim 2 wherein the ratio $R_5/R_{30} \leq 1.33$.
4. Structure according to any one of the preceding claims wherein the substrate is coated with an anticorrosion coating and the first coating layer is used as a tie coat over said anticorrosion coating.
5. Structure according to any one of the preceding claims wherein the biocide is one or more of a 2-trihalogenomethyl-3-halogeno-4-cyano pyrrole derivative substituted in position 5 and optionally in position 1, such as tralopyril, 1,4-dithiaanthraquinone-2,3-dicarbonitrile (dithianon), copper pyrithione, zinc pyrithione, tolylfluanid, dichlofluanid, and N-cyclopropyl-N'-(1,1-dimethylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine.
6. Structure according to any one of the preceding claims wherein the biocide in the first coating layer is an organic or metal-organic biocide.

7. Structure according to any one of the preceding claims wherein the biocide is one or more of a 2-trihalomethyl-3-halogeno-4-cyano pyrrole derivative substituted in position 5 and optionally in position 1 or 1,4-dithiaanthraquinone-2,3-dicarbonitrile.
- 5 8. Structure according to any one of the preceding claims wherein the subsequent coating layer(s) comprises an incompatible fluid.
9. Structure according to any one of the preceding claims wherein the substrate is
10 a marine or an aquaculture structure, such as, a ship hull, a boat hull, a buoy, a drilling platform, an oil rig, a floating production storage and offloading vessel (FPSO), a pipe, a cooling water intake in a power plant, a fish net or a fish cage.
10. Structure according to any one of the preceding claims wherein the structure is
15 a ship or boat hull, and the first coating layer is applied to result in a dry film thickness in the range of 100-200 μ m, and the subsequent coating layers(s) are applied to result in a dry film thickness in the range of 100-200 μ m.
11. A method of controlling the rate of release of biocide from a foul release coating
20 system, wherein the ratio of the release rate of biocide from the foul release coating system 5 days after application of the coating (R_5) and the release rate of biocide 30 days after application of the coating (R_{30}) $R_5/R_{30} \leq 1.5$, the method comprising
 - a. providing a substrate,
 - 25 b. coating the substrate with a first coating layer,
 - c. applying at least one subsequent coating layer on top of the first coating layer,
 the first coating layer formed from a coating composition containing a biocide, the subsequent coating layers(s) formed from coating composition(s) containing
30 less biocide than the coating composition forming the first coating layer and which is(are) free or substantially free of biocide, and wherein the first coating layer and the subsequent coating layer(s) comprise a polyorganosiloxane and fumed silica.
- 35 12. The method of claim 11, wherein the substrate is coated with an anticorrosion coating and the first coating layer is used as a tie coat over said anticorrosion coating.

13. The method of claim 11 or claim 12, wherein the biocide is one or more of a 2-trihalomethyl-3-halogeno-4-cyano pyrrole derivative substituted in position 5 and optionally in position 1, such as tralopyril, 1,4-dithiaanthraquinone-2,3-dicarbonitrile (dithianon), copper pyrrithione, zinc pyrrithione, tolylfluanid, dichlofluanid, and N-cyclopropyl-N'-(1,1-dimethylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine.
14. The method of any one of claims 11-13 wherein the subsequent coating layer(s) comprises an incompatible fluid.
15. The method of any one of claims 11-14 wherein the substrate is a marine or an aquaculture structure, such as, a ship hull, a boat hull, a buoy, a drilling platform, an oil rig, a floating production storage and offloading vessel (FPSO), a pipe, a cooling water intake in a power plant, a fish net or a fish cage and other aquaculture and marine apparatus or structures which are wholly or partially immersed in water.