Fouling release composition

The present invention relates to a fouling release composition comprising a cured or cross-linked polysiloxane and a fluorinated polymer or oligomer and a method for preventing fouling in an aquatic environment.

Background

Surfaces that are submerged in seawater are subject to fouling by marine organisms such as green algae, brown algae, barnacles, mussel, tube worms and the like. On marine constructions such as vessels, oil platforms, buoys etc. this fouling may result in increased load and accelerated corrosion. On vessels the fouling will reduce the manoeuvrability and increase the frictional resistance which will cause a reduction of the speed and increased fuel consumption.

To prevent attachment and growth of such marine organisms antifouling coatings are used. Traditional antifouling coatings prevent fouling on the surface by release of substances that are toxic to aquatic fouling organisms.

A more environmentally benign solution is the use of biocide-free fouling release coatings. These systems are effective due to the physical properties of the surfaces. Low surface energy, low glass transition temperature (T_g) and low elastic modulus of the surface makes it difficult for the organisms to adhere firmly to the surface, which reduce the accumulation of marine organisms.

The use of silicone elastomers, or silicone rubbers, for fouling release coatings has been known for some time, as disclosed in US 2,986,474, GB 1 307 001 and US 3,702,778. To improve the fouling release performance of the silicone coatings, chemically inert fluids additives are used. These additives migrate to the coating surface where they create a surface layer that promotes the release properties. GB 1 470 465 discloses the use of silicone oils in a curable silicone rubber formulation. GB 1 581 727 discloses the use of silicone-free fluid organic compounds, for example low molecular weight polyolefins, low molecular weight polydienes, mineral oils and plasticizers, in a vulcanised silicone rubber formulation. US 6,107,381 discloses the use of a non-curable polysiloxane comprising at least one polyoxyalkene moiety.

The fouling release coatings do not prevent fouling, but reduced the adhesion of fouling organisms on the surface. Some forces are needed to remove the attached fouling organisms from the surface. On a ship hull the hydrodynamic forces of the moving vessel have to be sufficiently high for an effective release of the fouling organisms. The silicone fouling release coatings is therefore limited to fast moving vessels with a speed of at least 15 knots. There is a need to improve the fouling release properties of these coatings, and the present invention offers a method for such improvement.

Perfluorinated compounds and polymers containing perfluorinated moieties are known for their very low surface energy and they can be used to improve the fouling release properties of silicone based systems. In a silicone system the fluorinated component will spontaneously migrate to the surface and accumulate at the polymer-air interface. Perfluoroalkyl groups will self-assembly on the surface stabilising the surface against reconstruction in water.

Fluorinated polymers and additives have been described for use in fouling release compositions. US 6,265,515 B1 (priority 1999, US Navy) discloses a curable fluorinated silicone resin and blends of the curable fluorinated silicone resin providing a low surface energy fouling release composition. The use of a cured or crosslinked polysiloxane and a fluorinated polymer or oligomer is not mentioned. EP1 042 413 B1 (priority GB 1997, Akzo) discloses a two-layer fouling release coating system where the outer layer comprising a curable polymeric fouling-inhibiting material, advantageously a curable polysiloxane, but other curable materials, especially fluorine-containing polymers may be used. The use of fluorine containing polymers in combination with a curable polysiloxane is not mentioned.

Arias E.M., et al., Polymer Preprints (1997), vol. 38, pp 512-513 describes a pure perfluorinated (meth)acrylate fouling release polymer. No fouling release compositions or use of the fluorinated polymers in combination with a curable polysiloxane are mentioned. US 6,899,955 B2 (priority EP 2000, Akzo) discloses a curable fluorinated resin, comprising a bifunctional fluorinated polyether having silicone end groups. Examples of additives that can be used in the coating composition are non- or monofunctional fluorinated polyethers. The use of fluorine containing polymers in combination with a curable polysiloxane is not mentioned. EP 1 377 643 B1 / US 2002/0192181 (priority EP 2001, Akzo) discloses a cured or cross-linked polymer and a non-reactive fluid fluorinated alkyl- or alkoxy-containing polymer or

oligomer. Polysiloxane is the preferred binder. The use of a fluorinated polymer or oligomer from ethylenically unsaturated monomers are not described.

The present invention provides a fouling release composition with improved fouling release properties comprising a cured or crosslinked polysiloxane and a fluorinated polymer or oligomer. The introduction of polysiloxane pendant groups in the fluorinated polymer or oligomer improves the compatibility with the polysiloxane coating formulation and facilitate the formation of a fluorinated surface layer. The perfluoroalkyl groups self-assembly on the surface stabilising the surface against reconstruction in water. This fluorinated layer can be further stabilised by introducing silane reactive groups in the fluorinated polymer or oligomer that can take part in the curing reaction of the polysiloxane coating.

The present invention represents a facile way to produce fluorinated polymers and oligomers, starting from commercial available products. It is possible to control the properties of the fluorinated polymer or oligomer such as surface energy, compatibility and reactivity in a polysiloxane blend by varying the monomer ratio and the chain length of the pendant groups.

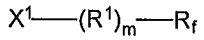
Fluorinated compounds have a relatively high cost. The present invention represent a way of improve the properties of a fouling release coating with a minimum amount of a fluorinated polymer.

The present invention provides a fouling release composition comprising a cured or crosslinked polysiloxane and a fluorinated polymer or oligomer. The present invention also relates to the use of the fouling release composition above in fouling release coatings for application to articles submerged in seawater.

DETAILED DESCRIPTION:

The fluorinated polymer or oligomer of the present invention relates to a polymer or oligomer comprising units selected from (A) polymerisable ethylenically unsaturated monomers containing fluorine functionality, optionally (B) polymerisable ethylenically unsaturated monomers containing polyorganosiloxane functionality and optionally (C) polymerisable ethylenically unsaturated monomers containing silane functionality, and optionally other polymerisable ethylenically unsaturated monomers.

Preferable, the fluorinated polymer or oligomer comprises units selected from monomer (A) of the general formula (I):



(I)

wherein

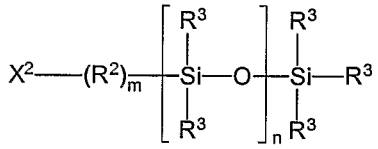
X^1 is an ethylenically unsaturated group, such as acryloyloxy, methacryloyloxy, vinyl or vinyloxycarbonyl

R^1 is a substituted or unsubstituted linear or branched C_1-C_{10} alkyl

m is 0 or 1

R_f is a perfluorinated linear or branched C_1-C_{20} alkyl;

optionally monomer (B) of the general formula (II):



(II)

wherein

X^2 is an ethylenically unsaturated group, such as acryloyloxy, methacryloyloxy or vinyl

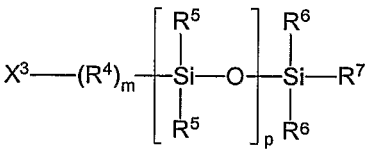
R^2 is a linear or branched C_1-C_{10} alkyl

R^3 is independently selected from C_1-C_{10} alkyl,

m is 0 or 1

n is an integer from 1 to 200;

and optionally monomer (C) of the general formula (III):



(III)

wherein

X^3 is an ethylenically unsaturated group, such as acryloyloxy, methacryloyloxy or vinyl
R^4 is a linear or branched C_1-C_{10} alkyl
m is 0 or 1
R^5 is a C_1-C_{10} alkyl,
R^6 is independently selected from C_1-C_{10} alkoxy and C_1-C_{10} alkyl,
R^7 is a C_1-C_{10} alkoxy,
p is 0 or 1;

and optionally one or more other polymerisable ethylenically unsaturated compounds.

The fluorinated polymer or oligomer of the present invention contains 1-99% by weight of monomer A, preferably 1-50% by weight of monomer A, especially preferred 1-25% by weight of monomer A. The fluorinated polymer or oligomer of the present invention contains 0-99% by weight of monomer B, preferably 1-99% by weight of monomer B. For monomer B (of the general formula (II)), n is preferably >1, more preferably n is >4 and especially preferably n is >8. The fluorinated polymer or oligomer of the present invention contains 0-25% by weight of monomer C.

Examples of monomer A include

1H,1H-perfluoropropyl acrylate, 1H,1H-perfluorobutyl acrylate, 1H,1H-perfluorooctyl acrylate, 1H,1H-perfluorooctyl methacrylate, 1H,1H-perfluorodecyl acrylate, 1H,1H-perfluorodecyl methacrylate, (perfluorocyclohexyl)methyl acrylate, (perfluorocyclohexyl)methyl methacrylate;

2-(perfluorobutyl)ethyl acrylate, 2-(perfluorobutyl)ethyl methacrylate, 2-(perfluorohexyl)ethyl acrylate, 2-(perfluorohexyl)ethyl methacrylate, 2-(perfluorooctyl)ethyl acrylate, 2-(perfluorooctyl)ethyl methacrylate, 2-(perfluorodecyl)ethyl acrylate, 2-(perfluorodecyl)ethyl methacrylate;

2-(perfluoro-3-methylbutyl)ethyl acrylate, 2-(perfluoro-3-methylbutyl)ethyl methacrylate, 2-(perfluoro-5-methylhexyl)ethyl acrylate , 2-(perfluoro-5-methylhexyl)ethyl methacrylate, 2-(perfluoro-7-methyloctyl)ethyl acrylate, 2-(perfluoro-7-methyloctyl)ethyl methacrylate, 2-(perfluoro-9-methyldecyl)ethyl acrylate, 2-(perfluoro-9-methyldecyl)ethyl methacrylate;

1H,1H,5H-perfluoropentyl acrylate, 1H,1H,5H-perfluoropentyl methacrylate, 1H,1H,7H-perfluoroheptyl acrylate, 1H,1H,7H-perfluoroheptyl methacrylate, 1H,1H,9H-perfluorononyl acrylate, 1H,1H,9H-perfluorononyl methacrylate, 1H,1H,11H-perfluoroundecyl acrylate, 1H,1H,11H-perfluoroundecyl methacrylate;

3-(perfluoro-3-methylbutyl)-2-hydroxypropyl acrylate, 3-(perfluoro-3-methylbutyl)-2-hydroxypropyl methacrylate, 3-(perfluoro-5-methylhexyl)-2-hydroxypropyl acrylate, 3-(perfluoro-5-methylhexyl)-2-hydroxypropyl methacrylate, 3-(perfluorobutyl)-2-hydroxypropyl acrylate, 3-(perfluorohexyl)-2-hydroxypropyl acrylate, 3-(perfluorohexyl)-2-hydroxypropyl methacrylate, 3-(perfluorooctyl)-2-hydroxypropyl acrylate, 3-(perfluorooctyl)-2-hydroxypropyl methacrylate;

vinyl perfluoroheptanoate, vinyl perfluorooctanoate, vinyl perfluorononanoate, p-vinylbenzyl perfluorooctanoate, 3-[2'-(perfluoropropoxy)-1',1',2'-trifluoroethoxy]vinylbenzene;
2-(perfluoropropoxy)perfluoropropyl trifluorovinyl ether

Examples of monomer B include
monomethacryloxypropyl terminated polydimethylsiloxane and monovinyl terminated polydimethylsiloxane. Preferred Mw 500-20 000, more preferred 800-10 000.

Examples of monomer C include
(3-acryloyloxypropyl)trimethoxysilane, (3-acryloyloxypropyl)methyldimethoxysilane, (3-acryloyloxypropyl)dimethylmethoxysilane, (3-methacryloyloxypropyl)triethoxysilane, (3-methacryloyloxypropyl)ethyldimethoxysilane,
(3-methacryloyloxypropyl)dimethyldiethoxysilane,

(methacryloyloxymethyl)trimethoxysilane, (methacryloyloxymethyl)triethoxysilane, (methacryloyloxymethyl)dimethylethoxysilane, (3-methacryloyloxypropyl)trimethoxysilane, (3-methacryloyloxypropyl)triethoxysilane, (3-methacryloyloxypropyl)methyldimethoxysilane, (3-methacryloyloxypropyl)ethyldimethoxysilane,
(3-methacryloyloxypropyl)dimethylmethoxysilane,
(3-methacryloyloxypropyl)dimethyldiethoxysilane,

vinyltrimethoxysilane, vinyltriethoxysilane, vinyltriisopropoxysilane, vinyltri-*tert*-butoxysilane, vinylmethyldimethoxysilane, vinylmethyldiethoxysilane,
vinyldimethylethoxysilane,
styrylethyltrimethoxysilane,

Examples of other ethylenically unsaturated compounds that may also be used in conformity with the invention are monomers such as acrylic acid and methacrylic acid, esters and amides of acrylic acid and methacrylic acid, vinyl compounds.

The fluorinated polymers according to the present invention may be prepared by polymerising at least one monomer A of the structure represented by formula (I) by a suitable polymerisation process.

The fluorinated polymer or oligomer of the present invention has a lower surface energy than the polysiloxane. In a blend of the fluorinated polymer or oligomer and polysiloxane the fluorinated polymer or oligomer will spontaneously migrate to the surface and accumulate at the polymer-air interface. This process 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 will improve the fouling release properties of the coating. In a coating comprising a fluorinated polymer or oligomer and a curable polysiloxane it is therefore desirable that the migration of the fluorinated polymer or oligomer to the surface is facilitated and that the fluorinated surface layer is stable. Since the fluorinated polymer or oligomer are generally incompatible with polysiloxane, this can prevent a controlled migration and of the fluorinated polymers or

oligomers to the coating surface and the formation of a fluorinated surface layer and instead result in the formation of fluorinated domains in polysiloxane matrix. The introduction of polysiloxane pendant groups in the fluorinated polymer or oligomer improves, the compatibility with the polysiloxane coating formulation and facilitate the formation of a fluorinated surface layer. When the fluorinated polymer or oligomer have migrated to the surface it is desirable to stabilise the surface of the coating against reconstruction and erosion of the outer fluorinated layer. Perfluoroalkyl groups will self-assembly on the surface stabilising the surface against reconstruction in water. This layer can be further stabilised by introducing silane reactive groups in the fluorinated polymer or oligomer that can take part in the curing reaction of the polysiloxane coating.

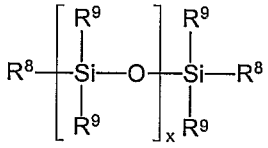
The preferred amount of the fluorinated polymer or oligomer is 0.1-25 % by weight of the curable polysiloxane.

The fouling release composition of the present invention comprises a cured or crosslinked polysiloxane. Preferably, the cured or crosslinked polysiloxane is a conventional room temperature vulcanizable (hereafter denoted RTV) composition generally consisting of the main components:

1) a reactive polysiloxane
2) a crosslinking agent
3) a condensation catalyst

The RTV composition can be a one-part or made up of several parts, but preferably not more than a three parts system.

The reactive polysiloxane of the present invention is a diorganosiloxane of the general formula (IV):



(IV)

wherein

R^8 is a hydroxyl or $-O-Si(R^{10})_y(R^{11})_{(3-y)}$

R^9 is independently selected from C_1-C_{10} alkyl, aryl and alkaryl

R^{10} is a hydroxy or a C_1-C_3 alkoxy

R^{11} is hydrogen or a C_1-C_3 alkyl,

y is an integer from 1 to 3.

Preferably, the reactive polysiloxane is a reactive polydimethylsiloxane.

The RTV composition may comprise one or more reactive silicone polymers differing in average molecular weight.

The crosslinking agent of the RTV composition has the general formula (V):

$$(R^{12})_z—Si—(X^4)_{(4-z)} \qquad (V)$$

wherein

X^4 is alkoxy, acetoxy, oxime, enoxy or amine

R^{12} is a C_1-C_{10} alkyl,

z is 0 or 1.

The crosslinking agent may be in a monomeric form or in the form of a self-condensation product, such as a dimer, oligomer or polymer.

If the polysiloxane is di- or tri-alkoxy terminated, a separate crosslinking agent is not required.

Curing of the silicone binder proceeds in the presence of a catalyst. Useful catalysts are those known to facilitate condensation reactions in RTV silicone systems, such as carboxylic salts of tin, zinc, titanium, lead, iron, barium and zirconium. Non-metallic catalysts such as hexylammonium acetate and benzyl trimethylammonium acetate, may also be employed.

A coating formulation comprising a fluorinated polymer or oligomer and a curable polysiloxane in accordance with the present invention may also include one or more non-reactive oils and other substances commonly used in coating formulation such as and fillers, pigments, solvents and additives:

Examples of non-reactive oils include silicone oils such as polydimethylsiloxane, methylphenyl silicone oils; organic oils such as polyolefin oils and paraffin and biological oils such as coconut oil.

Examples of fillers include barium sulphate, calcium sulphate, calcium carbonate, silicas, silicates, bentonites and other clays. The preferred fillers are silica, including hydrophobic and hydrophilic fumed silica and precipitated silica.

Examples of pigments include titanium dioxide, iron oxides, carbon black, lamp black, iron blue, phthalocyanine blue, cobalt blue, ultramarine blue, phthalocyanine green,

Examples of suitable solvents and diluents include aromatic hydrocarbons such as toluene, xylene, trimethylbenzene; aliphatic hydrocarbons such as white spirit; alcohols such as 1-methoxy-2-propanol, butanol; ketones such as 2,4-pentanedione, 4-methyl-2-pentanone, 5-methyl-2-hexanone, cyclohexanone; esters such as butyl acetate and mixtures of the above with one another or an aliphatic hydrocarbon.

The coating can be applied by any conventional method such as brushing, rolling or spraying (airless or conventional). The composition of the present invention can be applied onto any pre-treatment layers designed for polysiloxane based fouling release finish layers. Examples of such coating layers are epoxy anticorrosive layers and silicone-containing tie-layers designed to ensure adhesion between the substrate and the final silicone containing fouling release layer.

The following examples illustrate the present invention:

Example 1:

General procedure for preparation of fluorinated polymers

Solvent is charged to a reaction vessel equipped with stirrer, condenser, thermometer, an adding device and nitrogen inlet, and heated to 85°C under stirring. The monomer batch is prepared by charging the remaining solvents, the fluorinated monomer, other co-monomers and initiator in a flask or beaker. The monomer batch is then charged dropwise to the reaction vessel over a period of 2 hours. The reaction mixture is kept at 85°C for an additional 3 hours. Optionally, additional initiator in solvent may be added during the post reaction time or the temperature may be raised to 120°C for 30 minutes in order to consume any residual monomers.

The type and amount of monomers, solvent and initiator used for the preparation of the fluorinated polymers are given in table 1.

Table 1:

		P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12
Monomers (g)	1H,1H-perfluorodecyl acrylate	25.0											
	1H,1H,2H,2H-perfluorodecyl acrylate		23.7										
	1H,1H,2H,2H-perfluorodecyl methacrylate			24.2	13.8	23.2						24.0	23.8
	1H,1H,2H,2H-perfluorooctyl acrylate						20.1	61.4					
	1H,1H,2H,2H-perfluorooctyl methacrylate								20.6	59.0	20.5		
	Monomethacryloxypropyl terminated polydimethylsiloxane (Mw 800-1000)									41.0	79.5		
	Monomethacryloxypropyl terminated polydimethylsiloxane (Mw ~ 5000)	75.0	76.3	75.8			79.9	38.6	79.4			75.2	74.5
	Monomethacryloxypropyl terminated polydimethylsiloxane (Mw ~ 10000)				86.2	76.8							
	3-(Trimethoxysilyl)propyl											0.8	1.6

	methacrylate												
Solvent (g)	(Trifluoromethyl)benzene	150	150	150	150	150	150	150	150	150	150	150	150
Initiator (g)	AMBN	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50

Example 2:

Preparation of a three pack coating composition

Part A (base):

105.0 g polydimethylsiloxane, silanol terminated (visc. 1000 cSt)
18.0 g polydimethylsiloxane (visc. 100 cSt)
6.0 g titanium dioxide
1.0 g silica
60.0 g Xylene
6.5 g fluorinated polymer solution from example 1 (P1-P12)

Part B (curing agent)

5.0 g tetraethyl silicate

Part C (catalyst solution)

0.4 g dibutyltin diacetate
8.0 g Xylene

Example 3:

Testing of fouling release performance using pseudobarnacles

The coating compositions of Example 2 were applied by a frame applicator onto PVC panels primed with an epoxy primer and a tie-coat for silicone based coatings. The panels are allowed to cure for at least 1 day. Small aluminium studs (pseudobarnacles) are glued on to the surface using epoxy adhesive and cured for 5 days. The pseudobarnacles are removed by a shear force applied parallel to the surface using a hand-held force gauge. The force required to remove the pseudobarnacle is noted. The strength of adhesion is calculated by dividing the

shear force by the area of the pseudobarnacle base. The value reported is the average of 6 measurements.

The pseudobarnacle strength of adhesion for the coating compositions of Example 2 are given in table 2.

Table 2

Coating composition	Fluorinated polymer (Example 1)	Adhesion strength of shear (MPa)
C0	None	99
C1	P1	28
C2	P2	35
C3	P3	27
C4	P4	24
C5	P5	33
C6	P6	40
C7	P7	64
C8	P8	28
C9	P9	81
C10	P10	56
C11	P11	54
C12	P12	67

Patent claims

1. Fouling release composition comprising a cured or cross-linked polysiloxane and a fluorinated polymer or oligomer derived from an ethylenically unsaturated monomer.

2. Fouling release composition in accordance with claim 1, wherein the fluorinated polymer or oligomer comprises units selected from:

   (A) polymerisable ethylenically unsaturated monomers containing fluorine functionality;

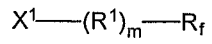
   optionally (B) polymerisable ethylenically unsaturated monomers containing polyorganosiloxane functionality;

   optionally (C) polymerisable ethylenically unsaturated monomers containing silane functionality; and

   optionally other polymerisable ethylenically unsaturated monomers.

3. Fouling release composition in accordance with claim 2, wherein the fluorinated polymer or oligomer comprises units selected from:

   monomer (A) of the general formula (I):



   (I)

   wherein

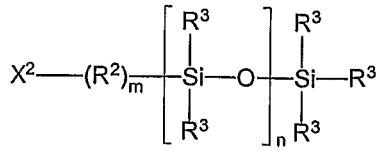
   X^1 is an ethylenically unsaturated group, such as acryloyloxy, methacryloyloxy, vinyl or vinyloxycarbonyl,

   R^1 is a substituted or unsubstituted linear or branched C_1-C_{10} alkyl,

   m is 0 or 1,

   Rf is a perfluorinated linear or branched C_1-C_{20} alkyl;

   optionally monomer (B) of the general formula (II):



(II)

wherein

X^2 is an ethylenically unsaturated group, such as acryloyloxy, methacryloyloxy or vinyl,

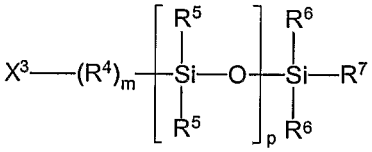
R^2 is a linear or branched C_1-C_{10} alkyl,

R^3 is independently selected from C_1-C_{10} alkyl,

m is 0 or 1,

n is an integer from 1 to 200;

optionally monomer (C) of the general formula (III):



(III)

wherein

X^3 is an ethylenically unsaturated group, such as acryloyloxy, methacryloyloxy or vinyl,

R^4 is a linear or branched C_1-C_{10} alkyl,

m is 0 or 1,

R^5 is a C_1-C_{10} alkyl,

R^6 is independently selected from C_1-C_{10} alkoxy and C_1-C_{10} alkyl,

R^7 is a C_1-C_{10} alkoxy,

p is 0 or 1;

and optionally one ore more other polymerisable ethylenically unsaturated compound.

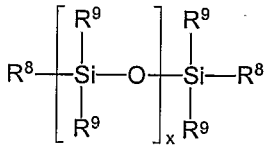
4. Fouling release composition in accordance with claim 3, wherein the fluorinated polymer or oligomer comprises 1-99% by weight of monomer A, 0-99% by weight of monomer B, and 0-25% by weight of monomer C.

5. Fouling release composition in accordance with claim 3, wherein the fluorinated polymer or oligomer comprises 1-50% by weight of monomer A, 0-99% by weight of monomer B, and 0-25% by weight of monomer C.

6. Fouling release composition in accordance with claim 3, wherein the fluorinated polymer or oligomer comprises 1-25% by weight of monomer A, 0-99% by weight of monomer B, and 0-25% by weight of monomer C.

7. Fouling release composition in accordance with claim 4-6, wherein the fluorinated polymer or oligomer comprises 1-99% by weight of monomer B.

8. Fouling release composition in accordance with claim 1-2, wherein the cured or crosslinked polysiloxane is a diorganosiloxane of the general formula (IV):



(IV)

wherein

R^8 is a hydroxyl or $-O\text{-}Si(R^{10})_y(R^{11})_{(3-y)}$,

R^9 is independently selected from C_1-C_{10} alkyl, aryl and alkaryl,

R^{10} is a hydroxy or a C_1-C_3 alkoxy,

R^{11} is hydrogen or a C_1-C_3 alkyl,

y is an integer from 1 to 3.

9. Fouling release composition in accordance with claim 1-8, wherein the cured or crosslinked polysiloxane is a reactive polydimethylsiloxane.

10. Fouling release composition in accordance with claim 1-8, wherein the amount of the fluorinated polymer or oligomer is 0.1-25 % by weight of the cured or crosslinked polysiloxane.

11. Use of a fouling release composition of any one of claims 1-10, in fouling release coatings for articles submerged in seawater.

12. Use in accordance with claim 11, wherein the articles are marine constructions such as vessels, oil platforms and buoys.