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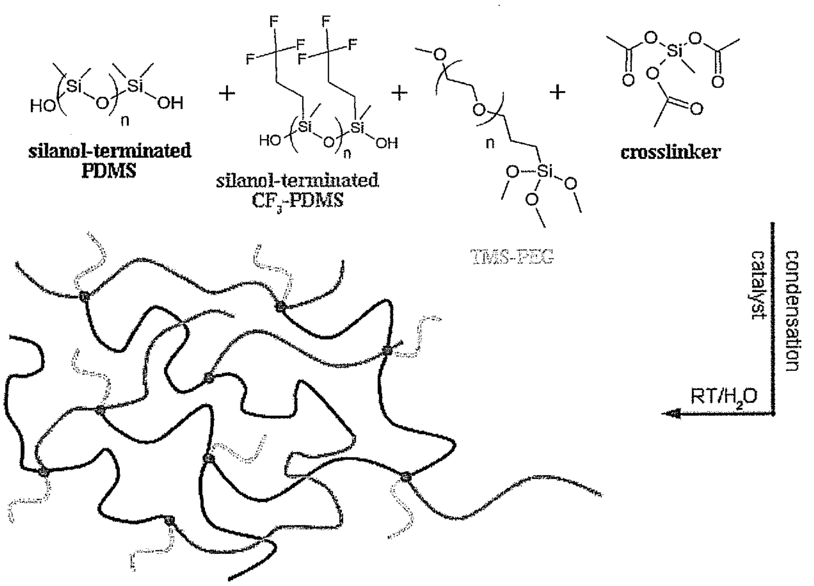
(54) Title: AMPHIPHILIC FOULING RELEASE COATINGS

Figure 1



(57) Abstract: The present invention provides an amphiphilic polymeric material well-suited as a coating for marine applications, such as use as a fouling-release coating on the external surfaces of ships, particularly ship hulls. Also provided are methods of making the polymeric material and methods for using the polymeric material, as well as articles and surfaces that are coated with the polymeric material.

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Amphiphilic Fouling Release Coatings

This application claims the benefit of U.S. Provisional Application Serial No. 61/283,522, filed December 4, 2009, which is incorporated herein by reference in its entirety.

Statement of Government Rights

This invention was made with government support under grants from the Office of Naval Research, Grant Nos. N00014-07-1-1099 and N00014-08-1-1149. The U.S. Government has certain rights in this invention.

Background of the Invention

Fouling of surfaces exposed to an aquatic environment is a serious problem. For example, surfaces of ships such as the hull, offshore marine structures such as oil rigs, sea water conduit systems for seaside plants, buoys, heat exchangers, cooling towers, desalination equipment, filtration membranes, docks, and the like may all experience some degree of fouling when continually exposed to water. In the case of ships, fouling can inhibit vessel performance and capabilities. For example, fouling may substantially increase fuel consumption and may necessitate extensive and more frequent maintenance, all of which raise the overall costs of operation. Fouling may also reduce ship speed, maneuverability, and range, which impede performance. On another level, attachment of regionally specific aquatic organisms on ships that traverse the world can lead to the unwanted invasion and infestation of these organisms to non-indigenous harbors. In some instances, this can have severe adverse effects on local aquatic ecosystems.

Over the years there have been numerous attempts to minimize the effect of fouling on structures exposed to an aquatic environment. For example, coatings (e.g., paints, etc.) have been developed that impede the attachment and/or growth of aquatic organisms on such structures. These coatings, commonly referred to as foul-release coatings, are typically silicone elastomers that possess a low surface energy such that the adhesion strength is relatively low and organisms can be readily removed by water jetting or moving the ship at high speed through the water. However, these coatings generally exhibit poor fouling-release of slimes. Moreover, the formulations typically include silicone oil, which eventually leaches from the coating, thereby reducing its effectiveness.

Summary of the Invention

The present invention provides an amphiphilic polymeric material for use in industrial and medical applications. The polymeric material is particularly well-suited as a coating for marine applications, such as use as a fouling-release coating on the external surfaces of ships, particularly ship hulls. Also provided are methods of making the polymeric material and methods for using the polymeric material, as well as articles and surfaces that are coated with the polymeric material or that otherwise include the polymeric material of the invention.

In one aspect, the invention provides a polymeric material formed by reacting a mixture that contains at least one hydrophilic component, at least one fluorine-containing component, and at least one silanol-terminated polysiloxane. Together, these constituent components advantageously impart amphiphilic character to the resulting polymeric material. Additionally, the polymeric material can be formed without the use of silicone oil. The hydrophilic component can be a polymer or a monomer. In one embodiment, the hydrophilic component is a hydrophilic polymer such as a polyalkylene glycol. In another embodiment, the hydrophilic component is a silane-functional compound. The silane-functional hydrophilic compound optionally includes a polymeric substituent. The fluorine-containing component can be a polymer or a monomer. In one embodiment, the fluorine-containing component is a silane-functional compound. The silane-functional fluorine-containing compound optionally includes a polymeric substituent. Silane-functional components optionally include an alkoxy group (e.g., they can be alkoxysilanes) which advantageously permits them to also function as crosslinking agents in the reaction mixture. The silanol-terminated polysiloxane can be a homopolymer, heteropolymer or copolymer, for example a block copolymer or a random copolymer. An exemplary silanol-terminated polysiloxane is silanol-terminated polydimethlylsiloxane.

The fluorine-containing component, hydrophilic component, and silanol-terminated polysiloxane can be separate components of the reaction mixture. Alternatively, any two of these constituents can constitute a single, bifunctional component. For example, a hydrophilic component and a fluorine-containing component can be constituents of a single, bifunctional copolymer. Likewise, at least one of the fluorine-containing component and the hydrophilic component can be part of a silanol-terminated polysiloxane.

The invention further provides fouling-release coatings, oils, films, and surface treatments formed from the polymeric material of the invention. Also provided are coated materials and surfaces, such as a substrate having a surface coated with a fouling-release coating that includes a polymeric material as described herein. Also provided are coated articles and objects, such as a maritime vessel coated with a fouling-release coating that includes a polymeric material as described herein.

In another aspect, the invention provides a method for making a polymeric material of that includes reacting at least one hydrophilic component, at least one fluorine-containing component, and at least one silanol-terminated polysiloxane under conditions to yield a polymeric material. Optionally, the method includes adding a crosslinking agent to react with the at least one hydrophilic component, at least one fluorine-containing component, and at least one silanol-terminated polysiloxane. The method further optionally includes the addition of a catalyst. The method can be carried out as a moisture cure process.

In another aspect, the invention provides a method for making a polymeric material that includes reacting at least one hydride- or vinyl-functionalized first component, at least one hydride- or vinyl-functionalized second component, and a hydride- or vinyl-functionalized silanol-terminated polysiloxane, wherein at least one of the first and second components comprises a hydrophilic group and at least one of the first and second components comprises a fluorine-containing group, under conditions to yield a polymeric material. The method can be carried out as an addition cure process.

In yet another aspect, the invention provides method for making a functionalized siloxane that includes reacting at least one hydride- or vinyl-functionalized first component, at least one hydride- or vinyl-functionalized second component, and a vinyl-or hydride-functionalized polysiloxane, wherein at least one of the first and second components includes a hydrophilic group and at least one of the first and second components includes a fluorine-containing group, under conditions to yield a functionalized siloxane. The functionalized siloxane can be a cyclic siloxane. A silanol-terminated polysiloxane can be formed by subjecting the functionalized cyclic siloxane to anionic ring-opening miniemulsion polymerization under conditions to yield a silanol-terminated polysiloxane. Advantageously, the silanol-terminated polysiloxane can take the form of an amphiphilic copolymer that includes at least one hydrophilic group at least one fluorine-containing group. A polymeric material can be formed by reacting the amphiphilic silanol-terminated polysiloxane with a polysiloxane such as polydimethylsiloxane.

In another aspect, the invention provides a method for protecting the surface of a substrate or article that includes coating the surface of the substrate or article with the polymeric material described herein. The invention further provides a method for facilitating the removal of a biofilm or marine organism from a substrate or article surface (such as the surface of a vessel) that includes coating the surface with a polymeric material as described herein.

Brief Descriptions of the Drawings

Figure 1 shows a general compositional space that is being investigated for the production of novel fouling-release coatings based the generation of amphiphilic surfaces.

Figure 2 shows fouling release data as a function of both CF_3-PDMS and TMS-PEG content.

Figure 3 shows biofilm retention, retraction, and removal data obtained using high-throughput assays and *C. lytica.*

Figure 4 shows biofilm retention and removal data obtained using high-throughput assays and *H. pacifica.*

Figure 5 shows cell attachment and removal obtained using high-throughput methods and *N. incerta.*

Figure 6 shows a barnacle reattachment assay. For the assay, 10 live, adult barnacles were used for each coating. The figure to the right displays the number of barnacles that would not attach to the coating surface.

Figure 7 shows images of a reattached barnacle removed from Intersleek 970 (IS 970) and a reattached barnacle removed from the coating containing the highest concentrations of TMS-PEG and CF_3-PDMS.

Figure 8 shows overall average rank obtained for fouling-release measurements as a function of coating composition.

Figure 9 shows a spider plot comparing of the experimental coating derived from the highest TMS-PEG and CF_3-PDMS content to Intersleek 970.

Figure 10 shows a synthetic scheme for generating amphiphilic polysiloxane coatings using commercially-available starting materials and an addition-cure mechanism.

Figure 11 shows a synthetic scheme for generating amphiphilic polysiloxane coatings using commercially-available starting materials and a moisture-cure mechanism. Hydrophilic groups are incorporated via the trimethoxysilane crosslinker.

Figure 12 shows a synthetic scheme for generating amphiphilic polysiloxane coatings using anionic ring-opening mini-emulsion polymerization (Barrere et al., Macromolecules, 2001, 34(21):7276-7280) to produce novel silanol-terminated amphiphilic polysiloxanes, followed by a moisture-cure mechanism to produce coatings.

Detailed Description of Illustrative Embodiments

Conventional polysiloxane fouling-release coatings provide good release of macrofoulers such as barnacles but exhibit poor fouling-release of slimes. The modified polysiloxanes of the invention show good fouling-release toward both barnacles and slimes. Also, conventional polysiloxane fouling-release coatings typically utilize a silicone oil in the formulation to enhance fouling-release properties. This silicone oil eventually leaves the coating and fouling-release performance is reduced. The modified polysiloxane coatings of the invention provide good fouling-release without the use of silicone oils which should enable long-lived fouling-release performance.

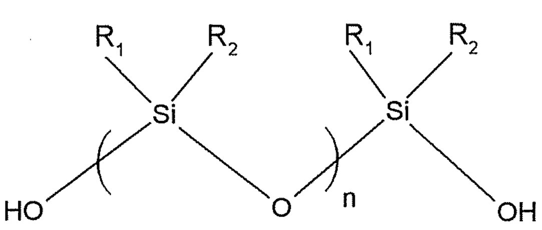
It has been found that incorporating hydrophilic moieties or segments and fluorine-containing moieties or segments into a moisture-curable polysiloxane coating results in a synergist enhancement in fouling-release properties toward a suite of marine organisms. In addition, the inclusion of the moieties does not negatively affect the mechanical properties of the coating after immersion in water.

The polymeric material of the invention is amphiphilic; that is, it contains both hydrophobic and hydrophilic moieties or segments. In a preferred embodiment, the polymeric material is formed by reacting a mixture containing at least one fluorine-containing component, at least one hydrophilic component, and at least one polysiloxane component, such as a silanol-terminated polysiloxane, under conditions to form the polymeric material. The polysiloxane component imparts hydrophobic character to the polymeric material. Amphiphilicity is incorporated into the polymeric material by either directly incorporating hydrophilic groups into a polysiloxane to yield a bifunctional amphiphilic polysiloxane, or through polymerization or cross-linking with one or more other reactive hydrophilic components. Likewise, the polymeric material is fluorine-containing by either directly incorporating fluorine atoms into a polysiloxane to yield a bifunctional fluorine-containing polysiloxane, or through polymerization or crosslinking with other reactive fluorine-containing components. In other words, and as described in more detail below, in some embodiments a fluorine-containing component and a polysiloxane component can take the form of a single component that is bifunctional; i.e., they do not need to be two separate components of the mixture. Likewise, in other embodiments, a hydrophilic component and a polysiloxane component may constitute a single component that is bifunctional. In yet other embodiments, a fluorine-containing component and a hydrophilic component may constitute a single component that is bifunctional. In yet other embodiments, two or more different fluorine-containing, hydrophilic and/or polysiloxane components may be included in the reaction mixture as desired. Regardless of how the various components are initially formulated, the resulting polymeric material is essentially a modified polysiloxane that contains both hydrophilic moieties or segments and fluorine-containing moieties or segments.

Examples of components that are useful to make the polymeric material of the invention, such as polysiloxanes, fluorine-containing components, or hydrophilic components, and reagents used to form the polymeric material, as well as examples of uses suitable for the polymeric material of the invention, are found in Chisholm et al., US Pat. Pub. 2007/0042199 published February 22, 2007, now issued as US Pat. No. 7,771,833, August 10, 2010, and Chisholm et al., US Pat. Pub. 2008/0181862, published July 31, 2008.

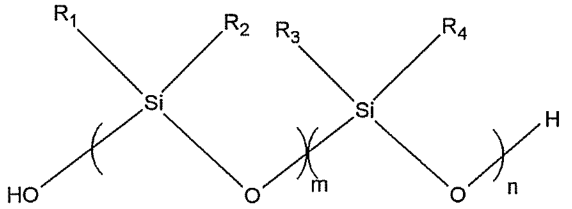
The polysiloxane component of the reaction mixture is preferably a silanol-terminated polysiloxane. In one embodiment, the silanol-terminated polysiloxane has an average molecular weight of at least about 5,000 g/mol. In another embodiment, the silanol terminated polysiloxane has an average molecular weight of about 10,000 g/mol to 100,000 g/mol or, suitably, about 15,000 g/mol to 75,000 g/mol. In yet another embodiment, the silanol terminated polysiloxane may have an average molecular weight of no more than about 150,000 g/mol. It should be appreciated, however, that the silanol terminated polysiloxane may have any suitable molecular weight and is not limited to any particular molecular weight or range of molecular weights described herein. The polysiloxane component can be linear, branched or cyclic. For example, the polysiloxane component can take the form of a silanol-terminated polydialkylsiloxane, a silanol-terminated polyalkylhydrosiloxane, or a silanol-terminated polysiloxane co-polymer, for example silanol-terminated polydimethylsiloxane(PDMS)-co-polymethylhydrosiloxane(PMHS).

In one embodiment, the silanol-terminated polysiloxane is a homopolymer having the general structure:



wherein R_1 and R_2 are each independently H, alkyl or aryl, provided at least one of R_1 and R_2 is alkyl or aryl, and n is about 1 to 5000, preferably about 5 to 2000. The alkyl group is preferably $(C_1\text{-}C_{10})$alkyl and can be saturated or unsaturated, linear, branched, or cyclic. Alkyl and aryl can be substituted or unsubstituted. Examples of suitable groups for incorporation into the silanol-terminated polysiloxane component as R_1 and/or R_2 include but are not limited to methyl, ethyl, phenyl, cyanopropyl, and trifluoropropyl. Silanol-terminated polydimethylsiloxane (PDMS) is an exemplary polysiloxane wherein both $R_1 = R_2$ = methyl; other exemplary polysiloxanes include silanol-terminated polymethylethylsiloxane, wherein R_1 = methyl and = R_2 = ethyl, and silanol-terminated polymethylphenylsiloxane wherein R_1 = methyl and R_2 = phenyl.

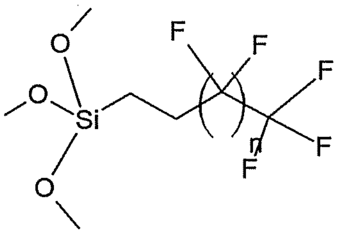
The polysiloxane component can alternatively be a heteropolymer that contains a plurality of different monomeric units. The pendent groups (R groups) in the heteropolymer may be the same or different, and may vary with the different monomeric units. The polysiloxane heteropolymer can take the form of a copolymer, which can be a block copolymer or a random copolymer. When formulated as a heteropolymer, at least one of the constituent monomeric units can advantageously contain a fluorine-containing or hydrophilic functionality, thereby assuming a dual role as the fluorine-containing component or the hydrophilic component of the mixture, in addition to serving as the polysiloxane component. As an example, when at least one R group is trifluoropropyl, the silanol-terminated polysiloxane may be bifunctional in that it may optionally serve as both the fluorine-containing component of the mixture and the silanol-terminated polysiloxane component. In this embodiment, the polysiloxane component can advantageously be formulated as a random or block copolymer having the structure:



wherein R_1, R_2, R_3 and R_4 are each independently H, alkyl or aryl, provided at least one of R_1 and R_2 is alkyl or aryl and at least one R_3 and R_4 a fluorine-containing moiety, for example trifluoropropyl, and wherein m and n are each independently about 1 to 5000, more preferably 2 to 500.

The fluorine-containing component of the mixture can be either polymeric or monomeric. In one embodiment, the fluorine-containing component takes the form of a silane-functional compound, e.g., a fluorine-containing silane, preferably a fluorine-containing alkoxysilane, such as a fluorine-containing dialkoxysilane or trialkoxysilane, including but not limited to fluorine-containing di- or trimethoxysilane, di-or triethoxysilane and di- or triacetoxysilane. Essentially any reactive silane can be fluorinated to yield the fluorine-containing component of the mixture. Silazanes and chlorosilanes can also be fluorinated to yield the fluorine-containing component of the mixture.

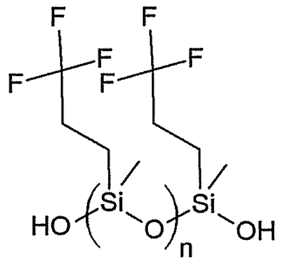
An example of a trimethoxysilane useful as a fluorine-containing component is:

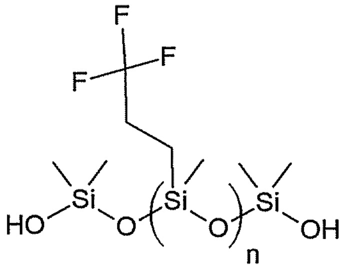


wherein n = 0 to about 20.

Many other exemplary fluorine-containing alkyl compounds which are useful as fluorine-containing components of the mixture, or as functional groups that can be used to derivatize silanes or other molecules in order to produce a fluorine-containing component for use in the reaction mixture, are described in Chisholm et al., US Pat. Pub. 2007/0042199 published February 22, 2007, the entirety of which is explicitly incorporated by reference.

In another embodiment, the fluorine-containing component of the mixture can take the form of a silanol-terminated fluorine-containing polysiloxane, such as silanol-terminated polytrifluoropropylmethylsiloxane (CF_3-PDMS). The silanol-terminated fluorine-containing polysiloxane preferably has a molecular weight of between 300 g/mol to 50,000 g/mol. Representative examples of silanol-terminated polytrifluoropropylmethylsiloxanes are shown below.



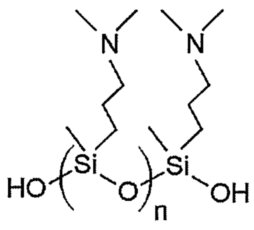


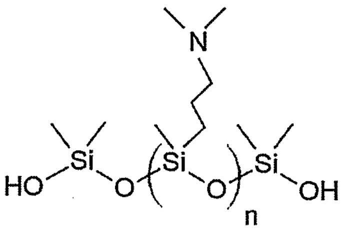
where n = 1 to about 500.

In some embodiments, a fluorine-containing polysiloxane copolymer can serve as both a fluorine-containing component and a silanol-terminated polysiloxane. More particularly, when formulated as a silanol-terminated random or block copolymer of fluorine-containing monomers and non-fluorine-containing monomers, a polysiloxane copolymer can serve as both a fluorine-containing component and as a silanol-terminated polysiloxane.

The hydrophilic component of the mixture can likewise be either polymeric or monomeric. In one embodiment, the hydrophilic component has a polymeric structure and can be, for example and without limitation, a polyalkylene glycol polymer or copolymer, such as polyethylene glycol, polyacrylic acid, polyhydroxyethyl acrylate, polyacrylamide, poly(2-(dimethylamino)ethyl acrylate, polymethacrylates such as polyhydroxyethyl methacrylate, polyethacrylates, maleic anhydride copolymers, poly(ethyleneglycols), poly(ethyleneoxides), polyamines, polyimines, poly(ethyleneimine), poly(vinylamine), poly(vinyl carboxylic acid amide) and other amine-functional polymers, polyethers, polystyrenes and polystyrenesulfonate, poly(methyl vinyl ether), polyvinyl acids, and polyvinyl alcohols, as well as derivatized forms thereof. A preferred polyalkylene hydrophilic component for use in the mixture has n repeating groups, with n = 1 to 100, more preferably n = 4 to 25.

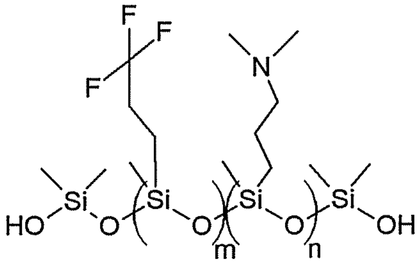
In another embodiment, the hydrophilic component of the reaction mixture can take the form of a silanol-terminated hydrophilic polysiloxane. A hydrophilic polysiloxane has been derivatized with a hydrophilic functional group, such as those described in more detail below, that imparts hydrophilic character to the polysiloxane. Representative examples of a silanol-terminated poly N,N-dimethylaminopropylmethylsiloxane is shown below:





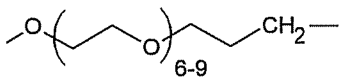
where n = 1 to about 500.

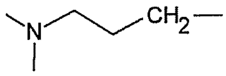
A representative bifunctional copolymer, which functions as both a hydrophilic component and a fluorine-containing component, is shown as below:

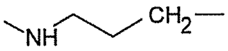


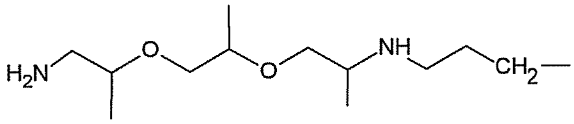
In another embodiment, the hydrophilic component of the mixture takes the form of a hydrophilic silane-functional component. A silane-functional hydrophilic component has preferably been derivatized with a functional group that imparts hydrophilic character to the silane. Silanes that can function as, or be further derivatized with one or more hydrophilic groups to function as, hydrophilic components for use in the reaction mixture include, for example, alkyoxysilanes, such as dialkoxysilanes or trialkoxysilanes, including but not limited to di- or trimethoxysilane, di-or triethoxysilane and di- or triacetoxysilane. Essentially any reactive silane can be derivatized with a hydrophilic moiety, or a repeating unit of a hydrophilic moiety, to yield a suitable hydrophilic component for use in the mixture. Silazanes and chlorosilanes can also be derivatized to yield the hydrophilic component of the mixture.

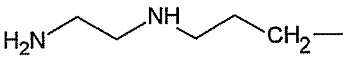
Hydrophilic functional groups that can be used to impart hydrophilicity to compounds such as silanes and polysiloxanes via covalent linkage to yield hydrophilic components suitable for use in the reaction mixture include, but not limited to, the following:

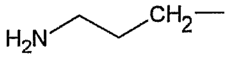






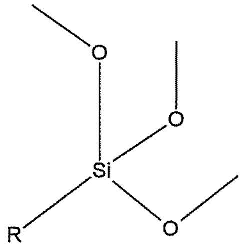






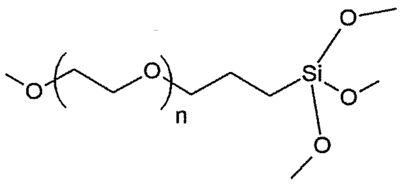
The hydrophilic functional group present on the hydrophilic component of the reaction mixture of the invention is optionally terminated with an alkoxy or hydroxy end cap group.

An example of a trimethoxysilane useful as a hydrophilic component of the reaction mixture of the invention is:



wherein the R group is a hydrophilic moiety, such as one of the functional groups described immediately above or a repeating unit of a hydrophilic moiety, such as a polyalkylene glycol, optionally terminated with an alkoxy or hydroxy end cap group.

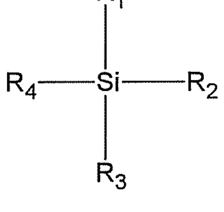
Another exemplary trimethoxysilane useful as a hydrophilic component of the reaction mixture of the invention is one that has been functionalized by covalent attachment of a hydrophilic polymer, such as polyethylene glycol or a derivative thereof. An example is trimethoxysilane-functional PEG (TMS-PEG), i.e., 2-[methoxy(polyethyleneoxy)propyl]-trimethoxysilane, where n = 1 to 20:



The hydrophilic component optionally includes an alkoxy group or hydroxy group. In a polymeric hydrophilic component, the alkoxy group or hydroxy group is preferably an end cap group, positioned at a terminus. Preferred terminal alkoxy groups include methoxy and ethoxy.

It will be generally appreciated that a silane-functional compound can be conveniently used for either or both of the fluorine-containing component(s) and/or the hydrophilic component(s) of the mixture. Advantageously, when formulated to contain at least one alkoxy group in addition to the fluorine-containing component(s) and/or the hydrophilic component(s), the silane-functional compound can further function as a crosslinking agent.

Generally, the silane-functional compound (as substituted silane) for use as a component in the mixture of the invention can take the form of:



wherein, in one embodiment, at least one of R_1, R_2, R_3, or R_4 is $-OR_5$, $-NHR_6$, or halide; R_5 is preferably H, alkyl, aryl, or $-C=OR_6$; and R_6 and R_7 are each independently preferably H, alkyl or aryl. At least one of R_1, R_2, R_3, or R_4 is optionally H. Substituents R_1, R_2, R_3 and R_4 on the silane-functional compound can aklyl or aryl, and can independently be saturated or unsaturated, linear, branched, or cyclic; substituted or unsubstituted. In one embodiment, at least one of R_1, R_2, R_3 and R_4 is alkoxy; more preferably, at least two of R_1, R_2, R_3 and R_4 are independently be alkoxy. In a particularly preferred embodiment, at least one of R_1, R_2, R_3, or R_4 can contain a monomor, oligomer or polymer, preferably a hydrophilic monomer, oligomer or polymer, or fluorine-containing hydrophilic monomer, oligomer or polymer as described hererin, and at least one, preferably two, of R_1, R_2, R_3, or R_4 are alkoxy.

The hydrophilic component(s), fluorine-containing component(s), and polysiloxane component(s) are preferably present in the mixture in the following weight percentages (wt %): hydrophilic component(s), 1 to 30 wt %, 2 to 25 wt%, or 5 to 20 wt%; fluorine-containing component(s), 3 to 80 wt%, 5 to 60 wt%, or 10-50 wt%, and the polysiloxane component(s), 0 to 80 wt%, 10 to 60 wt% or 20 to 50 wt%. Any lower limit can be combined with any upper limit to obtain a preferred range of weight percentages. It should be remembered that in some embodiments, a single component may have two functionalities (e.g., it may function as a fluorine-containing component and a polysiloxane component) and the weight percents can be adjusted accordingly.

The invention further includes a mixture containing one or more of the following reactants: one or more hydrophilic component(s) as described herein, one or more fluorine-containing component(s) as described herein, and/or one or more polysiloxane component(s) as described herein. The mixture optionally includes, either as a separate reactant or as a bifunctional component, a cross-linking agent. Also included are methods for making the polymeric material of the invention by reacting the components under conditions to form the polymeric material. In one embodiment of the method of making a polymeric material of the invention, the reaction components are contacted with a fumed silica dispersion in butyl acetate, and a catalyst. An exemplary catalyst is tetrabutylammonium fluoride. Other exemplary catalysts include organotin compounds such as dibutyltindiacetate or dibutyltindilaurate, 1,4-diazabicyclo[2.2.2]octane, triethylamine, tetrabutylammonium hydroxide The reactants can be added in any order to form the reaction mixture. In an exemplary method, the reactants are added in the any convenient order, such as this order: fluorine-containing component, polysiloxane component, fumed silica dispersion in butyl acetate, hydrophilic component, crosslinking agent, and catalyst. The reaction mixture is stirred, preferably at ambient temperature for a time sufficient to yield the polymeric material of the invention.

Polymer cross-linking is optionally enhanced by adding a cross-linking agent to the reaction mixture. Exemplary cross-linking agents include methyltriacetoxysilane, trialkoxysilane, and tetralkoxysilane. Some compounds, including derivatized silanes such as those described above and exemplified in Example III (e.g., derivatized trimethoxysilane), can concurrently serve as both a cross-linking agent and a hydrophilic component and/or a fluorine-containing component of the reaction mixture.

It should be noted that the mixture components shown in Examples I and II are formulated to function in a process that utilizes moisture curing. One of skill in the art will note, however, that the components can be readily reformulated to function in a process that utilizes addition curing, using reaction mixture components that have been functionalized to include one or more vinyl groups and/or a hydride, preferably a silyl hydride (SiH) functionality. Thus, in another embodiment, as exemplified in Example III, Fig. 10, the invention further includes a method for making the polymeric material of the invention using an addition cure process. Any of the fluorine-containing mixture components and/or hydrophilic reaction mixture components as described herein can be functionalized to contain one or more reactive vinyl groups and/or silyl hydride (SiH) functionality. In one embodiment of the addition cure method of the invention, vinyl-functionalized fluorine-containing and/or hydrophilic components are reacted with a hydride functionalized polysiloxane component that takes the form of a linear siloxane polymer or copolymer, such as a polyalkylhydrosiloxane or a polydiaklylsiloxane-co-polyalkylhydrosiloxane copolymer, or a cyclic. It should be understood that the vinyl functionality and the hydride functionality, which are both needed to participate in the addition cure reaction, can be incorporated into any of the reaction components as desired. The vinyl and hydride functionalities are typically incorporated into two or more different reaction components, but they can, if desired, be incorporated into the same component. The reaction is performed in the presence of a metal catalyst, such as platinum, to yield the polymeric material of the invention. An exemplary hydride functionalized linear siloxane copolymer contains first and second monomeric units–SiR_1R_2-O- and $-SiR_3R_4$-O-, respectively, wherein for the first monomer, $R_1=R_2=$alkyl, such as methyl; and for the second monomer, R_3=alkyl, such as methyl, and R_4=H. It should be understood that the polysiloxane component can, alternatively or additionally, contain one more vinyl functionalities. Optionally, at least one of the vinyl-functionalized or hydride functionalized fluorine-containing and/or hydrophilic polymeric components is a polymer. For example, the vinyl-functionalized fluorine-containing component can be a polysiloxane copolymer containing first and second monomeric units $-SiR_1R_2-O-$ and $-SiR_3R_4-O-$, respectively, wherein for the first monomer, $R_1 = R_2 =$ methyl; and for the second monomer, $R_3 =$ methyl and $R_4 =$ is a fluorine –containing group such as trifluoropropyl. An example of a suitable vinyl-functionalized hydrophilic component is vinyl-functionalized polyethylene glycol.

In another embodiment, the method of the invention can include preparation of a silanol-terminated functionalized polysiloxane copolymer using a hydrosilylation reaction, optionally followed by preparation of the polymeric material of the invention utilizing a moisture cure process; see, for example, Example III, Fig. 12. Advantageously, the hydrosilylation reaction can produce an amphiphilic polysiloxane, which can then be used as a bifunctional hydrophilic and fluorine-containing component in a moisture cure reaction to produce the polymeric material of the invention. A hydride-functionalized cyclic siloxane is reacted with at least one vinyl-functionalized reactant, which can be a vinyl-functionalized hydrophilic reactant and/or a vinyl-functionalized fluorine-containing reactant, in the presence of a metal catalyst, preferably platinum, to yield a functionalized cyclosiloxane. When at least one vinyl-functionalized hydrophilic reactant and at least one vinyl-functionalized fluorine-containing reactant are both used, the resulting functionalized cyclic siloxane is bifunctional. It should be understood that it does not matter which reactant contains the vinyl functionality and which reactant contains the hydride functionality; in other words, the reaction can occur using a vinyl-functionalized cyclic siloxane and at least one hydride-functionalized fluorine-containing reactant and/or at least one hydride-functionalized hydrophilic reactant. Examples of reactants that can be functionalized to contain a vinyl group or a hydride include compounds consisting of or containing any of the hydrophilic functional groups described herein and compounds consisting of or containing any of the fluorine-containing functional groups described herein. The derivatized cyclosiloxane intermediate is then exposed to a surfactant in the presence of an aqueous base in an anionic ring-opening reaction to yield a silanol-terminated polysiloxane oligomer or polymer. If both hydrophilic and fluorine-containing reactants were used, the product is a bifunctional silanol-terminated fluorine-containing hydrophilic polysiloxane oligomer, polymer, or copolymer. In that event, the resulting oligomer, polymer or copolymer can function as a bifunctional component, i.e., as both the fluorine-containing component and hydrophilic component, when included in the moisture cure reaction mixture of the invention. The resulting silanol-terminated oligomer, polymer or copolymer is then reacted with a polysiloxane, such as silanol-terminated polydimethylsiloxane, and optionally one or more other fluorine-containing and/or hydrophilic reaction mixture components, in the presence of a crosslinker such as an alkyoxysilane, to yield the polymeric material of the invention.

It should be understood that the invention generally includes methods for making hydrophilic component(s), fluorine-containing component(s), and polysiloxane component(s) of the mixture as described herein, as well as the hydrophilic component(s), fluorine-containing component(s), and polysiloxane component(s) thereby produced, as well methods for making the polymeric material of the invention and the polymeric material thereby produced, including methods described and exemplified in the Examples.

Methods of using the polymeric material of the invention are also included. The polymeric materials can be applied to coat or form surfaces of articles used in industrial, marine, and medical applications. Optionally a surface is treated with one or more base coats and/or one or more primer layers, in any order, prior to coating with the polymeric material of the invention.

A number of compounds suitable for use as or in anti-fouling materials are disclosed herein. In general, anti-fouling materials refer to products, agents, or compositions which may provide fouling release properties when used alone or in combination with other materials or substances. The anti-fouling materials described herein may include one or more of a number of suitable copolymers (e.g., block copolymers, graft copolymers, random copolymers, etc.) which provide fouling-release characteristics. Optionally, the polymeric material of the invention can include a functionalized polysiloxane that includes ionically or covalently bonded biocidal groups such as amines, quaternary amines, halides and the like.

The invention further contemplates preparations, formulations, coatings, films, oils, and composite materials that contain the polymeric material of the invention. Such materials are useful in many varied industrial and medical applications. Industrial applications include marine applications such as fouling-release treatments for surfaces of ships and boats such as the hull, offshore marine structures such as oil rigs, sea water conduit systems for seaside plants, buoys, heat exchangers, cooling towers, desalination equipment, filtration membranes, docks, aquatic zoo and aquarium and other structures which may all experience some degree of fouling when continually exposed to fresh or salt water. Medical applications include use as treatments for devices, including implantable devices, such as tubing, catheters, stents, vascular implants, cardiac regulation devices, and other devices that come into contact with body fluids.

Note that unless otherwise specified, "a," "an," "the," and "at least one" are used interchangeably and mean one or more than one.

Further, the present invention is illustrated by the following examples. It is to be understood that the particular examples, materials, amounts, and procedures are to be interpreted broadly in accordance with the scope and spirit of the invention as set forth herein.

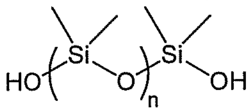
EXAMPLES

Example I

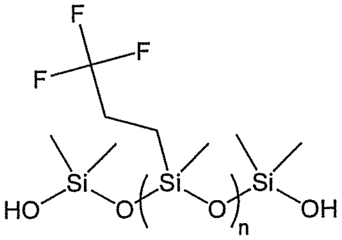
Amphiphilic Siloxane Fouling-Release Coatings

We report polysiloxane coatings that contain, in addition to polysiloxane chain segments, both hydrophilic moieties such as polyethylene glycol segments and fluorine-containing moieties. The coatings provide better fouling-release properties than analogous coatings that contain, in addition to polysiloxane chain segments, only hydrophilic moieties or only fluorine-containing moieties.

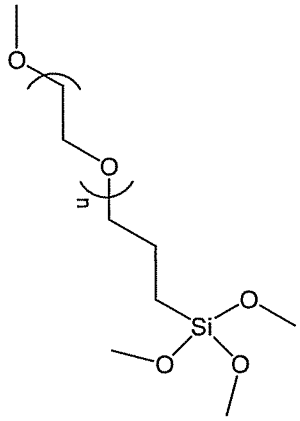
Exemplary components that were tested are shown below:



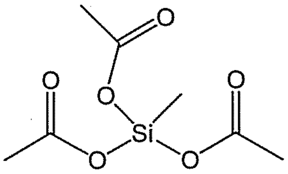
silanol-terminated
polydimethysiloxane



silanol-terminated
polytrifluoropropylmethylsiloxane



2-[methoxy(polyethyleneoxy)propyl]-trimethoxysilane



methyltriacetoxysilane

Table 1 describes the starting materials used to prepare the examples. Table 2 describes the compositions of the coating solutions prepared using an automated pipetting robot (Symx Viscous Formulation Station). Components were added in following order: FMS-9922, DMS-S35, fumed silica dispersion, butyl acetate, SIM6492.7, SIM6519.0, Catalyst solution. The coating solutions were mixed with magnetic stir bars in sealed containers at ambient conditions for approximately 16 hours. After mixing, coating specimens for evaluation of fouling-release properties were prepared by dispensing 200 microliter aliquots of coating solution into wells of a modified 24-well microtiter plate. The microtiter plate modification consisted of adhering 15 mm diameter coated aluminum discs to the bottom of the wells. The coated aluminum discs were prepared by sandblasting aluminum panels (3003 Q-panel) and then spraying International Paint Intergard 264 as a primer. From the primed aluminum panels, 15 mm discs were punched out using by a manual Unipunch press and a die. The discs were adhered to the well-bottoms of 24-well polystyrene plates (Falcon 35-1147 Sterile) with Dow Corning 734 adhesive. Next, 300 μL of a siloxane coating (Dow Corning 3140-MIL-A-46146) diluted by 50 wt. % with 4-methyl-2-pentanone was deposited into the wells to create a base coat on top of the primer layer and the base coat allowed to cure overnight.

Table 1. Description of the starting materials used to prepare the examples.

Tradename	Description	Manufacturer
FMS-9922	Silanol terminated Polytrifluorpropylmethylsiloxane (Mw 800-1200)	Gelest
DMS-S35	Silanol terminated Polydimethylsiloxane (Mw 49000)	Gelest
SIS6962.0	Hexamethyldisilazane treated fumed silica	Gelest
SIM6519.0	Methyltriacetoxysilane	Gelest
SIM6492.7 – 90%	2-[Methoxy(Polyethyleneoxy)propyl]-trimethoxysilane (EO repeats 6-9 units)	Gelest
216143	1 M Tetrabutylammonium fluoride in Tetrahydrofuran	Aldrich
Butyl acetate	Butyl acetate	Aldrich
4-methyl-2-pentanone	4-methyl-2-pentanone	Alfa Aesar

Specimens for mechanical property testing were prepared by solution casting films onto Teflon® sheet and subsequently stamping out test specimens of the cured coating films with a dumbbell-shaped die, type D, ASTM D412-98a. Specimens for barnacle reattachment assays were prepared by coating 3”x6” aluminum panels with both the Intergard 264 primer and Dow Corning 3140-MIL-A-46146 base coat as described above and then casting five milliliters of experimental coating solution over the substrate using an adjustable 2” doctor blade with a 25 mil wet film gap setting (Symyx Technologies).

Table 2. Composition of Examples and Reference materials.

Sample ID	FMS-9922	DMS-S35	Fumed Silica Dispersion*	butyl acetate	SIM6492.7 (90%)	SIM6519.0	Catalyst Solution **
Reference 1	0	12.22	6.29	9.9	0	1.53	1.88
Reference 2	0.51	11.55	6.29	9.9	0	1.53	1.88
Reference 3	1.03	10.88	6.29	9.9	0	1.53	1.88
Reference 4	1.54	10.21	6.29	9.9	0	1.53	1.88
Reference 5	2.06	9.54	6.29	9.9	0	1.53	1.88
Reference 6	0	11.95	6.14	10.02	0.32	1.49	1.88
Example 1	0.5	11.29	6.14	10.02	0.32	1.49	1.88
Example 2	1.01	10.63	6.14	10.02	0.32	1.49	1.88
Example 3	1.51	9.98	6.14	10.02	0.32	1.49	1.88
Example 4	2.01	9.32	6.14	10.02	0.32	1.49	1.88
Reference 7	0	11.68	6.01	10.14	0.62	1.46	1.88
Example 5	0.49	11.04	6.01	10.14	0.62	1.46	1.88

Example 6	0.98	10.4	6.01	10.14	0.62	1.46	1.88
Example 7	1.48	9.75	6.01	10.14	0.62	1.46	1.88
Example 8	1.97	9.11	6.01	10.14	0.62	1.46	1.88
Reference 8	0	11.43	5.87	10.26	0.91	1.43	1.88
Example 9	0.48	10.8	5.87	10.26	0.91	1.43	1.88
Example 10	0.96	10.17	5.87	10.26	0.91	1.43	1.88
Example 11	1.44	9.54	5.87	10.26	0.91	1.43	1.88
Example 12	1.92	8.91	5.87	10.26	0.91	1.43	1.88
Reference 9	0	11.18	5.75	10.36	1.19	1.4	1.88
Example 13	0.47	10.57	5.75	10.36	1.19	1.4	1.88
Example 14	0.94	9.95	5.75	10.36	1.19	1.4	1.88
Example 15	1.41	9.34	5.75	10.36	1.19	1.4	1.88
Example 16	1.88	8.72	5.75	10.36	1.19	1.4	1.88

All values are in milliliters. *Fumed silica dispersion was prepared by predispersing SIS6962.0 in butyl acetate at a 20/80 SIS6962.0/butyl acetate wt./wt. ratio. **Catalyst Solution was prepared by dissolving 216143 in 4-methyl-2-pentanone to a final concentration of 50 mM tetrabutylammonium fluoride.

The fouling-release properties of the examples and reference coatings described by Table 2 were evaluated using a suite of biological screening assays and the data is provided in Table 3.

An automated water jet methodology was used to rapidly evaluate the adhesion of two marine bacteria, *Cellulophaga lytica* and *Halomonas pacifica*, and a microalgae diatom, *Navicula incerta*, to coatings prepared in multi-well plates (Stafslien et al., *Review of Scientific Instrum.*, 2007, 78:1-6; Casse et al., *Biofouling*, 2007, 23(2):121-130). Briefly, 24 hour cultures of the marine bacteria in marine broth were harvested via centrifugation (10,000xg for 10 minutes) and rinsed three times with sterile artificial seawater (ASW). The bacteria were then re-suspended in artificial seawater (ASW) supplemented with 0.5 g/l of peptone (*C. lytica*)/dextrose (*H. pacifica*) and 0.1 g/l of yeast extract to achieve a final cell density of 10^7 to 10^8 cells/ml. Three day old cultures of *N. incerta* were rinsed three times with ASW and re-suspended in Guillard's F/2 medium to achieve a final cell density of 10^5 cells/ml. 1 ml of bacterial or microalgal suspension was added to each well of the coating plates and incubated at 28 °C for 24 hours and 18 °C for 2 hours, respectively. The plates were then transferred to the water jet apparatus and the coatings were subjected to water jet treatments at two different pressures, 10 and 20 psi for *C. lytica/N. incerta* and 15 and 25 psi for *H. pacifica*. Following water jet treatments, the coating plates containing bacteria were stained with crystal violet dye for 15 minutes, rinsed three times with ASW and imaged with a digital camera to enable percent surface coverage measurements for biofilm retraction calculations (Stafslien et al., *Biofouling*, 2007, 23(1):45-54). The crystal violet was extracted from the biofilms on the coating surfaces by adding 0.5 ml of 33% acetic acid for 15 minutes and the resulting eluates were transferred to a 96-well plate and measured for absorbance at 600 nm using a multi-well plate spectrophotometer. For the coating plates containing microalgae, the plates were immediately extracted after water jet treatments with 1.0 ml of dimethyl sulfoxide for 15 minutes. The resulting eluates were transferred to 96-well plates and measured for fluorescence of chlorophyll (Ex: 360 nm; Em: 670 nm). Percent removal calculations were determined by comparing the total biomass on the coating surfaces before and after water jet treatments as follows:

$$\% \text{ Removal} = (1-(\text{TBM}_J / \text{TBM}_{NJ})) \times 100$$

where; TBM_J = mean absorbance/fluorescence value of four replicate jetted samples, TBM_{NJ} = mean absorbance/fluorescence value of three replicate non-jetted samples.

The coatings prepared on 3” x 6” aluminium panels were evaluated for their ability to prevent or minimize the adhesion strength of barnacles using a rapid laboratory reattachment assay (Rittschof et al., *Biofouling*, 2008, 24(1):1-9). Nine adult barnacles (*Amphibalanus amphitrite*) of a testable size (>5mm basal diameter) were dislodged from silastic T2 panels and placed on the surface of the example and control coatings. The panels were then placed in a humid container for 48 hours to facilitate initial attachment and then transferred to an ASW aquarium tank system. The reattached barnacles were fed daily with freshly hatched brine shrimp nauplii (*Artemia* sp.). After 14 days of reattachment in the aquarium system, the coatings were removed and the barnacles were dislodged with a hand-held force gauge in shear to measure the peak force at release. Once the force gauge measurements were completed, the area of the barnacle base plates were measured using a Sigma Scan Pro software package and the adhesion strengths were calculated by dividing the force required to remove the barnacles by the basal area. Barnacle adhesion for each coating was reported as the mean value of the total number of

Table 3. Fouling-release data obtained from the biological laboratory assays.

Sample ID	Barnacle Reattachment (Mpa) 42 Days Water Immersion	C lytica Retraction % Coverage 7 days Preleach	C lytica Retraction % Coverage 28 days Preleach	N. incerta % removal 7 days Preleach	N. incerta % removal 28 days Preleach	H. pacifica % Removal 15 psi 7 days Preleach	H. pacifica % Removal 25 psi 7 days Preleach	H. pacifica % Removal 15 psi 28 days Preleach	H. pacifica % Removal 25 psi 28 days Preleach
Reference 1	0.16 ± 0.05	100 ± 0	99.3 ± 1.1	47.3 ± 4.5	53.1 ± 1.6	40.5 ± 2.9	51 ± 2.3	39.5 ± 2.6	54.2 ± 4.5
Reference 2	0.2 ± 0.03	100 ± 0.1	71.5 ± 40.9	33.2 ± 5.7	29.1 ± 5	35.3 ± 7.1	52.4 ± 2.4	47.8 ± 4.3	54 ± 1.1
Reference 3	0.21 ± 0.02	100 ± 0	58 ± 33.2	28.2 ± 1.1	25.8 ± 5.4	28.5 ± 1.3	56.6 ± 5	38.5 ± 11.4	39 ± 4.7
Reference 4	0.15 ± 0.04	99.2 ± 0.8	99.5 ± 0.9	45.6 ± 3.8	24.3 ± 4.5	23.2 ± 1.8	33.4 ± 7.4	28.2 ± 10	28.5 ± 3.4
Reference 5	0.15 ± 0.02	71.3 ± 2.4	25.5 ± 7.2	24.3 ± 5.1	16.2 ± 2.6	15.6 ± 2.6	34 ± 5.9	37.7 ± 5	53.1 ± 3.2
Reference 6	0.13 ± 0.03	100 ± 0	90.9 ± 7.7	31.9 ± 6.1	56 ± 7.7	32.9 ± 4.7	31.8 ± 9.7	16.3 ± 4.6	29 ± 5.3
Example 1	0.13 ± 0.04	25 ± 20.3	56.1 ± 3	22.7 ± 7.9	25.4 ± 5.8	19.7 ± 5	28.7 ± 4.1	21.4 ± 5.2	25.3 ± 7.1
Example 2	0.17 ± 0.03	10.9 ± 2.6	19.1 ± 8.5	30.5 ± 11.1	19 ± 2.2	16.4 ± 3.3	36.8 ± 4.8	39.8 ± 4	48.8 ± 10.4
Example 3	0.14 ± 0.04	5.9 ± 0.3	15.9 ± 1.8	48.2 ± 7.9	40.5 ± 6	16.6 ± 9.5	26 ± 10.4	20.6 ± 10.9	22.8 ± 10.5
Example 4	0.12 ± 0.05	28.8 ± 4.6	6.3 ± 1.6	49.6 ± 3.2	14 ± 16.8	69.9 ± 12.4	85.3 ± 5.6	51 ± 7.1	63.4 ± 3.7
Reference 7	0.11 ± 0.06	100 ± 0	100 ± 0	35.2 ± 2.9	28.8 ± 2.5	3.2 ± 10.7	11.6 ± 1.6	30.9 ± 37.8	61.5 ± 2.7
Example 5	0.13 ± 0.02	10.6 ± 3.9	17.7 ± 3.9	23.3 ± 10.1	42 ± 6.6	19.2 ± 4.9	41.6 ± 2.4	32.9 ± 10.8	31.9 ± 2.7
Example 6	0.12 ± 0.05	29.1 ± 14.4	24.9 ± 7	40.1 ± 10.3	37.4 ± 7	21.2 ± 6.8	33.5 ± 9.2	30.2 ± 5.2	35.3 ± 5.2
Example 7	0.12 ± 0.03	16.9 ± 3	19 ± 5	49.7 ± 2.8	31.1 ± 12.6	50.5 ± 4.3	56.4 ± 2.4	36.6 ± 5.6	66.7 ± 9.9
Example 8	0.11 ± 0.04	25.8 ± 24.6	1.4 ± 0.8	31.8 ± 13	45.7 ± 10.7	54.5 ± 12.7	73.8 ± 7.4	45.2 ± 3.5	50.7 ± 3.5
Reference 8	0.12 ± 0.03	97.7 ± 3.9	99.1 ± 1.6	14.2 ± 3.4	5.5 ± 3.3	24.4 ± 4.2	33.5 ± 1.8	29.6 ± 4.6	48.4 ± 8.5
Example 9	0.14 ± 0.03	50.6 ± 16	20.3 ± 2.2	62.5 ± 7.2	39.4 ± 9.7	20.8 ± 3.8	24.6 ± 4	16 ± 8.3	26.2 ± 3.5
Example 10	0.10 ± 0.04	60.2 ± 7.6	14 ± 3.1	46.3 ± 4.2	28.6 ± 6.9	35.4 ± 3.6	39.7 ± 3.4	15.2 ± 6.8	28.4 ± 3.9
Example 11	0.09 ± 0.02	53 ± 26	37.2 ± 10.3	53.2 ± 13.8	44.1 ± 6.2	62.5 ± 7.1	82.4 ± 5.5	53.8 ± 3.7	75.1 ± 0.8
Example 12	0.13 ± 0.02	15.1 ± 12.4	5.2 ± 4.7	73.3 ± 2.8	58 ± 17.7	41.1 ± 9.4	43.2 ± 8	31.6 ± 15.4	45.3 ± 8.6
Reference 9	0.11 ± 0.04	75.9 ± 17.1	68.2 ± 31	18.1 ± 6	29.1 ± 4.8	1 ± 0.1	24.8 ± 6.3	20.8 ± 8.9	18 ± 5.8
Example 13	0.08 ± 0.04	16 ± 15.6	17.8 ± 12.7	1 ± 0.5	46.5 ± 7	21.4 ± 4.8	38.2 ± 2.2	37.2 ± 3	33.5 ± 17.8
Example 14	0.12 ± 0.05	24.8 ± 2.5	22.2 ± 4.7	60.6 ± 15.8	43.3 ± 11.5	51.5 ± 3.1	50.9 ± 0.7	17.4 ± 14.1	17.3 ± 7.6
Example 15	0.09 ± 0.05	28.6 ± 37.8	8.9 ± 9.2	55 ± 11.4	38.4 ± 7.6	67.5 ± 3.8	61.8 ± 1.7	36.3 ± 10	41.8 ± 7.8
Example 16	0.06 ± 0.06	8.8 ± 0.7	6 ± 1.3	42.3 ± 10.5	36.9 ± 2.3	72.2 ± 20.3	102.2 ± 12.9	66.6 ± 10.6	78.8 ± 2.2

barnacles that had a measurable detachment force. Barnacles that had no measurable force for detachment were counted as "not attached," and not included in adhesion calculations.

To facilitate analysis of the fouling release data, Tables 5 - 13 were generated using the format shown in Table 4. The matrix shown in Table 4 displays variations in coating composition as a function of two components, namely, SIM6492.7 and FMS-9922. Moving from top to bottom in the matrix corresponds to a relative increase in the amount of SIM6492.7 in the coating; while moving across the matrix from left to right corresponds to an increase of FMS-9922 in the coating. The low level (0) for both components corresponds to a composition that does not contain that component. Tables 5–13 are reproductions of the matrix shown in Table 4 with the exception that the sample identification (e.g. Reference 1, Example 3, etc.) has been replaced by the average and standard deviation of a given response obtained for that sample. For example, in Table 5, the value of "25 ± 20.3" is percent biofilm coverage obtained for "Example 1;" in Table 5, the value of "10.9 ± 2.6" is percent biofilm coverage obtained for "Example 2;" and so on.

Table 4. Matrix used for analyzing fouling-release data.

SIM6492.7	FMS-9922 Level				
Level	0	1	2	3	4
0	Reference 1	Reference 2	Reference 3	Reference 4	Reference 5
1	Reference 6	Example 1	Example 2	Example 3	Example 4
2	Reference 7	Example 5	Example 6	Example 7	Example 8
3	Reference 8	Example 9	Example 10	Example 11	Example 12
4	Reference 9	Example 13	Example 14	Example 15	Example 16

Table 5 displays the fouling-release data obtained from the bacterial biofilm retraction assay based on *C. lytica*. As described by Stafslien et al. (Stafslien et al., *Biofouling*, 2007, 23(1):45-54), this lower coating surface coverage by the biofilm corresponds to enhanced fouling-release performance. From Table 5, it can be seen that after preleaching coatings for 7 days all of the Example coatings which contained both SIM6492.7 and FMS-9922 displayed lower biofilm surface coverage (i.e. better fouling-release) than its corresponding Reference coatings that contained the same level of either SIM6492.7 or FMS-9922. For example, the surface coverage for Example 1 was lower than either Reference 2 or Reference 6; the surface coverage for Example 6 was lower than either Reference 2 or Reference 7; the surface coverage for Example 11 was lower than that of Reference 4 or Reference 8; and so on. As shown in Table 6, after preleaching the samples for 28 days, the same general result was obtained as obtained with samples preleached for 7 days.

Table 5. Fouling-release data obtained from the bacterial biofilm retraction assay based on *C. lytica*. Coatings were preleached for 7 days prior to testing. All values are in percent.

SIM6492.7 Level	FMS-9922 Level				
	0	1	2	3	4
0	100 ± 0	100 ± 0.1	100 ± 0	99.2 ± 0.8	71.3 ± 2.4
1	100 ± 0	25 ± 20.3	10.9 ± 2.6	5.9 ± 0.3	28.8 ± 4.6
2	100 ± 0	10.6 ± 3.9	29.1 ± 14.42	16.9 ± 3	25.8 ± 24.6
3	97.7 ± 3.9	50.6 ± 16	60.2 ± 7.6	53 ± 26	15.1 ± 12.4
4	75.9 ± 17.1	16 ± 15.6	24.8 ± 2.5	28.6 ± 37.8	8.8 ± 0.7

Table 6. Fouling-release data obtained from the bacterial biofilm retraction assay based on *C. lytica*. Coatings were preleached for 21 days prior to testing. All values are in percent.

SIM6492.7 Level	FMS-9922 Level				
	0	1	2	3	4
0	99.3 ± 1.1	71.5 ± 40.9	58 ± 33.2	99.5 ± 0.9	25.5 ± 7.2
1	90.9 ± 7.7	56.1 ± 3	19.1 ± 8.5	15.9 ± 1.8	6.3 ± 1.6
2	100 ± 0	17.7 ± 3.9	24.9 ± 7	19 ± 5	1.4 ± 0.8
3	99.1 ± 1.6	20.3 ± 2.2	14 ± 3.1	37.2 ± 10.3	5.2 ± 4.7
4	68.2 ± 31	17.8 ± 12.7	22.2 ± 4.7	8.9 ± 9.2	6 ± 1.3

Tables 7, 8, 9, and 10 display fouling-release data in matrix format for experiments conducted using the marine bacterium, *H. pacifica*. Overall, the data obtained with this assay show that, in general, Examples possessing SIM6492.7 and FMS-9922 at levels of 3 or 4 exhibit better *H. pacifica* removal than their corresponding Reference coatings that possess either SIM6492.7 or FMS-9922 at the same concentration level. Also, independent of preleach time or water-jet pressure, Examples 11 and 16 showed higher *H. pacifica* removal than any of the Reference coatings.

Table 7. *H. pacifica* removal data for samples preleached for 7 days. The water-jet pressure used was 15 psi. All values are in percent.

SIM6492.7 Level	FMS-9922 Level				
	0	1	2	3	4
0	40.5 ± 2.9	35.3 ± 7.1	28.5 ± 1.3	23.2 ± 1.8	15.6 ± 2.6
1	32.9 ± 4.7	19.7 ± 5	16.4 ± 3.3	16.6 ± 9.5	69.9 ± 12.4

2	3.2 ± 10.7	19.2 ± 4.9	21.2 ± 6.77	50.5 ± 4.3	54.5 ± 12.7
3	24.4 ± 4.2	20.8 ± 3.8	35.4 ± 3.6	62.5 ± 7.1	41.1 ± 9.4
4	1 ± 0.1	21.4 ± 4.8	51.5 ± 3.1	67.5 ± 3.8	72.2 ± 20.3

Table 8. *H. pacifica* removal data for samples preleached for 7 days. The water-jet pressure used was 25 psi. All values are in percent.

SIM6492.7	FMS-9922 Level				
Level	0	1	2	3	4
0	51 ± 2.3	52.4 ± 2.4	56.6 ± 5	33.4 ± 7.4	34 ± 5.9
1	31.8 ± 9.7	28.7 ± 4.1	36.8 ± 4.8	26 ± 10.4	85.3 ± 5.6
2	11.6 ± 1.6	41.6 ± 2.4	33.53 ± 9.23	56.4 ± 2.4	73.8 ± 7.4
3	33.5 ± 1.8	24.6 ± 4	39.7 ± 3.4	82.4 ± 5.5	43.2 ± 8
4	24.8 ± 6.3	38.2 ± 2.2	50.9 ± 0.7	61.8 ± 1.7	102.2 ± 12.9

Table 9. *H. pacifica* removal data for samples preleached for 28 days. The water-jet pressure used was 15 psi. All values are in percent.

SIM6492.7	FMS-9922 Level				
Level	0	1	2	3	4
0	39.5 ± 2.6	47.8 ± 4.3	38.5 ± 11.4	28.2 ± 10	37.7 ± 5
1	16.3 ± 4.6	21.4 ± 5.2	39.8 ± 4	20.6 ± 10.9	51 ± 7.1
2	30.9 ± 37.8	32.9 ± 10.8	30.23 ± 5.2	36.6 ± 5.6	45.2 ± 3.5
3	29.6 ± 4.6	16 ± 8.3	15.2 ± 6.8	53.8 ± 3.7	31.6 ± 15.4
4	20.8 ± 8.9	37.2 ± 3	17.4 ± 14.1	36.3 ± 10	66.6 ± 10.6

Table 10. *H. pacifica* removal data for samples preleached for 28 days. The water-jet pressure used was 25 psi. All values are in percent.

SIM6492.7	FMS-9922 Level				
Level	0	1	2	3	4
0	54.2 ± 4.5	54 ± 1.1	39 ± 4.7	28.5 ± 3.4	53.1 ± 3.2
1	29 ± 5.3	25.3 ± 7.1	48.8 ± 10.4	22.8 ± 10.5	63.4 ± 3.7
2	61.5 ± 2.7	31.9 ± 2.7	35.28 ± 5.17	66.7 ± 9.9	50.7 ± 3.5
3	48.4 ± 8.5	26.2 ± 3.5	28.4 ± 3.9	75.1 ± 0.8	45.3 ± 8.6
4	18 ± 5.8	33.5 ± 17.8	17.3 ± 7.6	41.8 ± 7.8	78.8 ± 2.2

Tables 11 and 12 display fouling-release data obtained using the marine algal species, *N. incerta*. In general, the results displayed in these two tables show that Examples possessing SIM6492.7 and FMS-9922 levels of 2 or higher exhibit better *N. incerta* removal than their corresponding References that possess either SIM6492.7 or FMS-9922 at the same concentration level.

Table 11. Fouling-release data obtained using the marine algal species, *N. incerta*. Coating were preleached for 7 days prior to testing. Water-jet pressure was 10 psi. All values are in percent.

SIM6492.7 Level	FMS-9922 Level				
	0	1	2	3	4
0	47.3 ± 4.5	33.2 ± 5.7	28.2 ± 1.1	45.6 ± 3.8	24.3 ± 5.1
1	31.9 ± 6.1	22.7 ± 7.9	30.5 ± 11.1	48.2 ± 7.9	49.6 ± 3.2
2	35.2 ± 2.9	23.3 ± 10.1	40.1 ± 10.3	49.7 ± 2.8	31.8 ± 13
3	14.2 ± 3.4	62.5 ± 7.2	46.3 ± 4.2	53.2 ± 13.8	73.3 ± 2.8
4	18.1 ± 6	1 ± 0.5	60.6 ± 15.8	55 ± 11.4	42.3 ± 10.5

Table 12. Fouling-release data obtained using the marine algal species, *N. incerta*. Coating were preleached for 28 days prior to testing. Water-jet pressure was 10 psi. All values are in percent.

SIM6492.7 Level	FMS-9922 Level				
	0	1	2	3	4
0	53.1 ± 1.6	29.1 ± 5	25.8 ± 5.4	24.3 ± 4.5	16.2 ± 2.6
1	56 ± 7.7	25.4 ± 5.8	19 ± 2.2	40.5 ± 6	14 ± 16.8
2	28.8 ± 2.5	42 ± 6.6	37.38 ± 7.03	31.1 ± 12.6	45.7 ± 10.7
3	5.5 ± 3.3	39.4 ± 9.7	28.6 ± 6.9	44.1 ± 6.2	58 ± 17.7
4	29.1 ± 4.8	46.5 ± 7	43.3 ± 11.5	38.4 ± 7.6	36.9 ± 2.3

Table 13 displays results in matrix form for barnacle adhesion. In general, Examples possessing relatively high levels of both SIM6492.7 and FMS-9922 showed better barnacle removal (i.e. lower barnacle adhesion strength) than any of the References.

Table 13. Fouling-release data obtained using the barnacle reattachment assay. Coatings were preleached for 42 days prior to testing. All values are in MPa.

SIM6492.7 Level	FMS-9922 Level				
	0	1	2	3	4
0	0.16 ± 0.05	0.2 ± 0.03	0.21 ± 0.02	0.15 ± 0.04	0.15 ± 0.02
1	0.13 ± 0.03	0.13 ± 0.04	0.17 ± 0.03	0.14 ± 0.04	0.12 ± 0.05
2	0.11 ± 0.06	0.13 ± 0.02	0.12 ± 0.05	0.12 ± 0.03	0.11 ± 0.04
3	0.12 ± 0.03	0.14 ± 0.03	0.1 ± 0.04	0.09 ± 0.02	0.13 ± 0.02
4	0.11 ± 0.04	0.08 ± 0.04	0.12 ± 0.05	0.09 ± 0.05	0.06 ± 0.06

The mechanical properties of coating films were determined according to ASTM 882-02 both before and after immersing in tap water for 24 hours. As shown in Table 14, in general, immersion of the Examples in water did not significantly reduce the mechanical properties.

Table 14. Mechanical properties of coating films before and after immersion in water.

Sample ID	Modulus (Mpa) before immersion	Elongation before immersion	Energy to Break before immersion	Tensile Strength (Mpa) before immersion	Modulus (Mpa) after immersion	Elongation after immersion	Energy to Break after immersion	Tensile Strength (Mpa) after immersion
Reference 1	0.8 ± 0.1	261.9 ± 47.91	1.08 ± 0.37	1.33 ± 0.25	0.68 ± 0.14	271.67 ± 0.67	1.17 ± 0.55	1.43 ± 0.4
Reference 2	0.61 ± 0.02	370.37 ± 58.02	2.03 ± 0.8	2.03 ± 0.55	0.57 ± 0.06	275.67 ± 0.3	1.12 ± 0.23	1.47 ± 0.23
Reference 3	0.84 ± 0.08	290.65 ± 63.99	1.62 ± 0.82	1.9 ± 0.71	0.85 ± 0.04	324.73 ± 0.58	2.18 ± 0.83	2.37 ± 0.57
Reference 4	0.79 ± 0.08	319.93 ± 108.86	2.01 ± 1.14	1.93 ± 0.74	0.76 ± 0.03	340.1 ± 0.45	2.22 ± 0.55	2.2 ± 0.3
Reference 5	0.69 ± 0.02	393.33 ± 57.41	2.49 ± 0.63	1.87 ± 0.25	0.75 ± 0.05	369.57 ± 0.46	2.12 ± 0.45	1.7 ± 0.17
Reference 6	0.73 ± 0.04	338.5 ± 21.46	1.81 ± 0.25	1.9 ± 0.17	0.73 ± 0.02	262 ± 0.81	1.15 ± 0.61	1.4 ± 0.52
Example 1	0.83 ± 0.03	372.73 ± 27.17	2.34 ± 0.3	2.17 ± 0.15	0.82 ± 0.05	340.13 ± 0.81	1.85 ± 0.83	1.77 ± 0.45
Example 2	0.93 ± 0.05	360.27 ± 29.86	2.31 ± 0.3	2 ± 0.1	0.99 ± 0.09	372.83 ± 0.38	2.45 ± 0.43	2.07 ± 0.12
Example 3	0.76 ± 0.04	362.4 ± 25	1.89 ± 0.25	1.57 ± 0.12	0.77 ± 0.02	315.17 ± 0.13	1.41 ± 0.1	1.27 ± 0.06
Example 4	0.53 ± 0.01	362.73 ± 17.59	1.33 ± 0.14	1.07 ± 0.06	0.53 ± 0.02	304.63 ± 0.32	0.93 ± 0.15	0.87 ± 0.06
Reference 7	0.79 ± 0.07	274.9 ± 17.61	1.3 ± 0.18	1.63 ± 0.15	0.84 ± 0.08	264.03 ± 0.66	1.28 ± 0.53	1.57 ± 0.4
Example 5	1.04 ± 0.04	268.63 ± 16.67	1.32 ± 0.16	1.47 ± 0.06	1 ± 0.02	272 ± 0.06	1.33 ± 0.05	1.47 ± 0.06
Example 6	0.99 ± 0.09	300.35 ± 24.79	1.51 ± 0.21	1.48 ± 0.11	0.97 ± 0.04	300.82 ± 0.14	1.49 ± 0.13	1.46 ± 0.07
Example 7	0.89 ± 0.03	237.57 ± 17.42	0.81 ± 0.1	0.97 ± 0.06	0.86 ± 0.03	191.67 ± 0.19	0.52 ± 0.08	0.73 ± 0.06
Example 8	0.46 ± 0.08	358.53 ± 69.97	1.16 ± 0.38	0.93 ± 0.15	0.53 ± 0.06	343.8 ± 0.92	1.14 ± 0.51	0.93 ± 0.21
Reference 8	0.58 ± 0.04	340.63 ± 19.27	1.67 ± 0.21	1.73 ± 0.12	0.63 ± 0	317.73 ± 0.31	1.49 ± 0.35	1.63 ± 0.31
Example 9	0.95 ± 0.08	312.5 ± 21.83	1.63 ± 0.2	1.57 ± 0.12	0.86 ± 0.01	311.1 ± 0.2	1.56 ± 0.18	1.57 ± 0.12
Example 10	1.26 ± 0.02	191.9 ± 14.19	0.68 ± 0.09	0.93 ± 0.06	1.08 ± 0.04	198.2 ± 0.15	0.68 ± 0.08	0.93 ± 0.06
Example 11	0.75 ± 0.01	286.13 ± 12.6	1.03 ± 0.09	1.03 ± 0.06	0.73 ± 0.07	256.07 ± 0.23	0.79 ± 0.12	0.87 ± 0.06
Example 12	0.5 ± 0.01	388.67 ± 31.34	1.37 ± 0.22	1.07 ± 0.12	0.57 ± 0.05	248.67 ± 0.43	0.63 ± 0.17	0.7 ± 0.1
Reference 9	0.82 ± 0.03	200.63 ± 2.9	0.66 ± 0.02	1 ± 0	0.89 ± 0.08	159.27 ± 0.02	0.46 ± 0.01	0.9 ± 0
Example 13	1.05 ± 0.1	263.13 ± 24.57	1.22 ± 0.24	1.33 ± 0.15	1.06 ± 0.18	225.57 ± 0.39	0.89 ± 0.27	1.17 ± 0.21
Example 14	0.74 ± 0.02	441.4 ± 8.01	2.45 ± 0.16	1.7 ± 0.1	0.84 ± 0.08	337.07 ± 0.79	1.61 ± 0.6	1.43 ± 0.29
Example 15	0.62 ± 0.03	354.67 ± 47.77	1.42 ± 0.3	1.23 ± 0.12	0.57 ± 0.01	433.4 ± 0.13	1.99 ± 0.06	1.4 ± 0
Example 16	0.61 ± 0.02	357.97 ± 66.22	1.35 ± 0.43	1.1 ± 0.17	0.7 ± 0.13	265.03 ± 1.16	0.82 ± 0.6	0.77 ± 0.29

Example II

Amphiphilic Siloxane Fouling-Release Coatings

Table 15 describes the starting materials used to prepare the examples. Table 16 describes the compositions of the coating solutions prepared using an automated pipetting robot (Symyx Viscous Formulation Station). Components were added in following order: FMS-9922, DMS-S35, fumed silica dispersion, butyl acetate, SIM6492.7, SIM6519.0, Catalyst solution. The coating solutions were mixed with magnetic stir bars in sealed containers at ambient conditions for approximately 16 hours. After mixing, coating specimens for evaluation of fouling-release properties were prepared by dispensing 200 microliter aliquots of coating solution into wells of a modified 24-well microtiter plate. The microtiter plate modification consisted of adhering 15 mm diameter coated aluminum discs to the bottom of the wells. The coated aluminum discs were prepared by sandblasting aluminum panels (3003 Q-panel) and then spraying International Paint Intergard 264 as a primer. From the primed aluminum panels, 15 mm discs were punched out using by a manual Unipunch press and a die. The discs were adhered to the well-bottoms of 24-well polystyrene plates (Falcon 35-1147 Sterile) with Dow Corning 734 adhesive. Next, 300 µL of a siloxane coating (Dow Corning 3140-MIL-A-46146) diluted by 50 wt. % with 4-methyl-2-pentanone was deposited into the wells to create a base coat on top of the primer layer and the base coat allowed to cure overnight.

Specimens for mechanical property testing were prepared by solution casting films onto Teflon® sheet and subsequently stamping out test specimens of the cured coating films with a dumbbell-shaped die, type D, ASTM D412-98a. Specimens for barnacle reattachment assays were prepared by coating 4”x8” aluminum panels with both the Intergard 264 primer and Dow Corning 3140-MIL-A-46146 base coat as described above and then casting eight milliliters of experimental coating solution over the substrate using an adjustable doctor blade with a 50 mil wet film gap setting (Paul N. Gardner Company, Inc).

Table 15. Description of the starting materials used to prepare the examples.

Tradename	Description	Manufacturer
FMS-9922	Silanol terminated Polytrifluorpropylmethylsiloxane (Mw 800-1200)	Gelest
DMS-S35	Silanol terminated Polydimethylsiloxane (Mw 49000)	Gelest
SIS6962.0	Hexamethyldisilazane treated fumed silica	Gelest
SIM6519.0	Methyltriacetoxysilane	Gelest
SIM6492.7 – 90%	2-[Methoxy(Polyethyleneoxy)propyl]-trimethoxysilane (EO repeats 6-9 units)	Gelest
216143	1 M Tetrabutylammonium fluoride in Tetrahydrofuran	Aldrich
Butyl acetate	Butyl acetate	Aldrich
4-methyl-2-pentanone	4-methyl-2-pentanone	Alfa Aesar

Table 16. Composition of Examples and Reference materials.

Sample ID	FMS-9922	DMS-S35	Fumed Silica Dispersion*	butyl acetate	SIM6492.7 (90%)	SIM6519.0	Catalyst Solution**
Reference 1	0	24.43	12.56	19.78	0	3.06	3.75
Reference 2	2.06	21.76	12.57	19.8	0	3.06	3.75
Reference 3	2.58	21.1	12.58	19.81	0	3.06	3.76
Reference 4	3.09	20.42	12.57	19.81	0	3.06	3.75
Reference 5	3.59	19.65	12.51	19.7	0	3.04	3.73
Reference 6	4.11	19.04	12.55	19.77	0	3.05	3.75
Reference 7	4.63	18.4	12.57	19.8	0	3.06	3.75
Reference 8	6.31	21.74	15.42	24.29	0	3.75	4.6
Reference 9	6.99	21.06	15.52	24.45	0	3.78	4.63
Reference 10	0	22.95	11.8	20.6	1.83	2.87	3.77
Example 1	1.93	20.38	11.78	20.56	1.83	2.87	3.76
Example 2	2.41	19.75	11.77	20.55	1.82	2.86	3.76
Example 3	2.9	19.14	11.79	20.58	1.83	2.87	3.76
Example 4	3.31	18.14	11.55	20.17	1.79	2.81	3.69
Example 5	3.88	17.95	11.83	20.66	1.83	2.88	3.78
Example 6	4.34	17.25	11.78	20.57	1.83	2.87	3.76
Example 7	5.92	20.38	14.45	25.23	2.24	3.52	4.62
Example 8	6.55	19.74	14.55	25.4	2.26	3.54	4.65
Reference 11	0	22.39	11.51	20.75	2.38	2.8	3.76
Example 9	1.89	19.93	11.51	20.75	2.38	2.8	3.76
Example 10	2.36	19.3	11.51	20.75	2.38	2.8	3.76
Example 11	2.83	18.72	11.53	20.78	2.38	2.81	3.76

Example 12	3.3	18.1	11.52	20.78	2.38	2.8	3.76
Example 13	3.77	17.47	11.52	20.77	2.38	2.8	3.76
Example 14	4.25	16.86	11.52	20.77	2.38	2.8	3.76
Example 15	5.8	19.96	14.15	25.52	2.93	3.44	4.62
Example 16	6.42	19.34	14.26	25.7	2.95	3.47	4.65

All values are in milliters. *Fumed silica dispersion was prepared by predispersing SIS6962.0 in butyl acetate at a 20/80 SIS6962.0/butyl acetate wt./wt. ratio. **Catalyst Solution was prepared by dissolving 216143 in 4-methyl-2-pentanone to a final concentration of 50 mM tetrabutylammonium fluoride.

The fouling-release properties of the examples and reference coatings described by Table 16 were evaluated using a suite of biological screening assays and the data is provided in Table 17.

An automated water jet methodology was used to rapidly evaluate the adhesion of two marine bacteria, *Cellulophaga lytica* and *Halomonas pacifica*, and a microalgae diatom, *Navicula incerta*, to coatings prepared in multi-well plates (Stafslien et al., *Review of Scientific Instrum.*, 2007, 78:1-6; Casse et al., *Biofouling*, 2007, 23(2):121-130). Briefly, 24 hour cultures of the marine bacteria in marine broth were harvested via centrifugation (10,000xg for 10 minutes) and rinsed three times with sterile artificial seawater (ASW). The bacteria were then re-suspended in artificial seawater (ASW) supplemented with 0.5 g/l of peptone (*C. lytica*)/dextrose (*H. pacifica*) and 0.1 g/l of yeast extract to achieve a final cell density of 10^7 to 10^8 cells/ml. Three day old cultures of *N. incerta* were rinsed three times with ASW and re-suspended in Guillard's F/2 medium to achieve a final cell density of 10^5 cells/ml. 1 ml of bacterial or microalgal suspension was added to each well of the coating plates and incubated at 28 °C for 24 hours and 18 °C for 2 hours, respectively. The plates were then transferred to the water jet apparatus and the coatings were subjected to water jet treatments at two different pressures, 10 and 20 psi for *C. lytica* and *N. incerta* and 15 and 25 psi for *H. pacifica*. Following water jet treatments, the coating plates containing bacteria were stained with crystal violet dye for 15 minutes, rinsed three times with ASW, and imaged with a digital

Table 17. Fouling-release data obtained from the biological laboratory assays.

Sample ID	Barnacle Reattachment (Mpa) 28 Days Water Immersion	Barnacle Reattachment # of Non attached barnacle 28 Days Water Immersion	C lytica Retraction % Coverage 28 days Preleach	C lytica % removal 10 psi 28 days Preleach	C lytica % removal 20 psi 28 days Preleach	N. incerta % removal 10 psi 28 days Preleach	N. incerta % removal 20 psi 28 days Preleach	H. pacifica % Removal 15 psi 28 days Preleach	H. pacifica % Removal 25 psi 28 days Preleach
Reference 1	0.23 ± 0.03	1	100 ± 0	35.1 ± 7.3	48.1 ± 3.8	25 ± 12.5	39.3 ± 5.5	15.6 ± 6.7	6.6 ± 6.7
Reference 2	0.18 ± 0.04	0	99.8 ± 0.3	46.1 ± 1.9	53.2 ± 1	4.7 ± 2.5	29.3 ± 3.7	4.8 ± 3.6	5.2 ± 3.9
Reference 3	0.16 ± 0.03	0	99.9 ± 0.1	55 ± 2.8	67.1 ± 4.2	12.4 ± 2.2	32.1 ± 1	27.3 ± 5.9	20.9 ± 9.9
Reference 4	0.16 ± 0.03	0	100 ± 0	40.6 ± 4.7	56.4 ± 3.6	17.4 ± 16	33.2 ± 4.1	4.6 ± 8.2	0 ± 15.5
Reference 5	0.18 ± 0.02	0	99.8 ± 0.3	40.3 ± 1.2	52.6 ± 3.1	13.3 ± 0.3	38.3 ± 5.4	12.4 ± 5.7	23.3 ± 5.6
Reference 6	0.15 ± 0.02	0	99 ± 1	37.9 ± 5.4	54.8 ± 1.5	18.4 ± 1.5	39.3 ± 7.7	21.9 ± 9	30.8 ± 10.8
Reference 7	0.13 ± 0.07	0	88.9 ± 7.6	41.6 ± 2.7	54.3 ± 6.9	19.9 ± 3.2	35.4 ± 2	11.9 ± 3.1	15.3 ± 6.7
Reference 8	0.15 ± 0.03	1	97.9 ± 2.9	45.7 ± 6.9	63.7 ± 0.8	12.2 ± 2.9	35.8 ± 2.6	12.1 ± 5.8	9.2 ± 4.5
Reference 9	0.15 ± 0.05	3	93 ± 4.7	50.9 ± 7.7	67.4 ± 5.5	21.7 ± 3.3	39.2 ± 3.3	31.6 ± 6	52.4 ± 3.1
Reference 10	0.13 ± 0.03	0	100 ± 0.1	36.6 ± 3.1	42.2 ± 11.5	8.9 ± 1.5	31.3 ± 2.6	15.2 ± 2.5	26.1 ± 5.7
Example 1	0.13 ± 0.03	2	5.4 ± 3	85.6 ± 5.2	91.6 ± 3.2	24.5 ± 1.6	39.2 ± 7.9	15 ± 2.1	16.1 ± 6.3
Example 2	0.1 ± 0.04	1	1.9 ± 1.3	93.1 ± 1.3	97.3 ± 1	33.7 ± 23.8	54.1 ± 11.2	0 ± 14.3	0 ± 14.3
Example 3	0.11 ± 0.04	2	4.2 ± 3.6	95.8 ± 0.9	97.3 ± 0.8	22.2 ± 4	43 ± 5.5	25 ± 7.2	33.1 ± 2.1
Example 4	0.13 ± 0.02	3	13.5 ± 23.1	96.3 ± 2.8	99.8 ± 1.4	20 ± 19.9	39.9 ± 15.5	14.4 ± 7	15.8 ± 8.1
Example 5	0.08 ± 0.05	3	0.1 ± 0.1	97.1 ± 1.8	98.5 ± 0.7	25.1 ± 11.3	33.4 ± 6.6	21.4 ± 5.2	41.5 ± 15.7
Example 6	0.07 ± 0.03	2	0.8 ± 1.1	93.6 ± 6.9	94.3 ± 8.4	25.1 ± 15.3	37.9 ± 11.5	24.6 ± 5.2	29.4 ± 3.4
Example 7	0.1 ± 0.02	5	0.5 ± 0.4	93.9 ± 2.3	94.6 ± 3.6	17.1 ± 6.6	36.2 ± 6	72.5 ± 0.5	84.8 ± 1.5
Example 8	0.08 ± 0.02	6	2.4 ± 1.6	95.8 ± 2.8	98 ± 0.6	23.2 ± 5.7	52.4 ± 3.3	48.4 ± 6.7	49.6 ± 4.9
Reference 11	0.15 ± 0.04	1	92.7 ± 2.5	30.9 ± 1.9	42.5 ± 1.4	14.3 ± 2.3	34.1 ± 5.4	0 ± 26.8	0 ± 26.8
Example 9	0.11 ± 0.03	0	9.4 ± 9.6	94.8 ± 2	97.8 ± 0.7	23.7 ± 2.4	44.4 ± 6.5	2.1 ± 6.9	0 ± 7.7
Example 10	0.08 ± 0.04	3	1.7 ± 0.1	96 ± 0	96.1 ± 3.1	17 ± 4.3	37.5 ± 8.4	37.1 ± 8.5	27.3 ± 7.2
Example 11	0.09 ± 0.04	3	0.6 ± 0.6	96.7 ± 0.7	99.1 ± 0.5	18.2 ± 11.6	39 ± 10.7	8.5 ± 2.8	16.3 ± 3.5
Example 12	0.08 ± 0.04	3	3.2 ± 1.1	95.9 ± 0.4	99 ± 0.4	15.2 ± 4	41.6 ± 3	50 ± 1.8	52.5 ± 6.3
Example 13	0.09 ± 0.01	7	20 ± 10	94.7 ± 2	97.2 ± 2.1	16.2 ± 4.9	47.3 ± 0.7	28.4 ± 15.7	59.9 ± 12.4
Example 14	0.17 *	8	9.6 ± 4.5	92.3 ± 5.3	96.8 ± 2.4	13.1 ± 9.2	47.7 ± 10.7	57.4 ± 2.5	63.9 ± 4.2
Example 15	0.08 ± 0.03	7	8.2 ± 5	97.3 ± 0.3	97 ± 0.6	23.3 ± 6.5	51.2 ± 2.9	87.6 ± 19	98.4 ± 3.6
Example 16	0.05 ± 0.02	5	13.1 ± 2.2	99.6 ± 0.2	100 ± 0.3	29.9 ± 2.6	49.6 ± 3.1	80.9 ± 5.5	100 ± 8.3

* Only one measurement was acquired due to inability of barnacles to attach to these surfaces

camera to enable percent surface coverage measurements for biofilm retraction calculations (Stafslien et al., *Biofouling*, 2007, 23(1):45-54). The crystal violet was extracted from the biofilms on the coating surfaces by adding 0.5 ml of 33% acetic acid for 15 minutes and the resulting eluates were transferred to a 96-well plate and measured for absorbance at 600 nm using a multi-well plate spectrophotometer. For the coating plates containing microalgae, the plates were immediately extracted after water jet treatments with 1.0 ml of dimethyl sulfoxide for 15 minutes. The resulting eluates were transferred to 96-well plates and measured for fluorescence of chlorophyll (Ex: 360 nm; Em: 670 nm). Percent removal calculations were determined by comparing the total biomass on the coating surfaces before and after water jet treatments as follows:

$$\% \text{ Removal} = (1-(TBM_J / TBM_{NJ})) \times 100$$

where; TBM_J = mean absorbance/fluorescence value of four replicate jetted samples, TBM_{NJ} = mean absorbance/fluorescence value of three replicate non-jetted samples.

The coatings prepared on 4" x 8" aluminium panels were evaluated for their ability to prevent or minimize the adhesion strength of barnacles using a rapid laboratory reattachment assay (Rittschof et al., *Biofouling*, 2008, 24(1):1-9). Nine adult barnacles (*Amphibalanus amphitrite*) of a testable size (>5mm basal diameter) were dislodged from silastic T2 panels and placed on the surface of the example and control coatings. The panels were then placed in a humid container for 48 hours to facilitate initial attachment and then transferred to an ASW aquarium tank system. The reattached barnacles were fed daily with freshly hatched brine shrimp nauplii (*Artemia* sp.). After 28 days of reattachment in the aquarium system, the coatings were removed and the barnacles were dislodged with a hand-held force gauge in shear to measure the peak force at release. Once the force gauge measurements were completed, the area of the barnacle base plates were measured using a Sigma Scan Pro software package and the adhesion strengths were calculated by dividing the force required to remove the barnacles by the basal area. Barnacle adhesion for each coating was reported as the mean value of the total number of barnacles that had a measurable detachment force. Barnacles that had no measurable force for detachment were counted as "not attached", and not included in adhesion calculations.

To facilitate analysis of the fouling release data, Tables 19 - 27 were generated using the format shown in Table 18. The matrix shown in Table 18 displays variations in coating composition as a function of two components, namely, SIM6492.7 and FMS-9922. Moving from top to bottom in the matrix corresponds to a relative increase in the amount of SIM6492.7 in the coating; while moving across the matrix from left to right corresponds to an increase of FMS-9922 in the coating. The low level (0) for both components corresponds to a composition that does not contain that component. Tables 19 – 27 are reproductions of the matrix shown in Table 18 with the exception that the sample identification (e.g. Reference 1, Example 3, etc.) has been replaced by the average and standard deviation of a given response obtained for that sample. For example, in Table 19, the value of "5.4 ± 3" is percent biofilm coverage obtained for "Example 1;" in Table 19, the value of "1.9 ± 1.3" is percent biofilm coverage obtained for "Example 2;" and so on.

Table 19 displays the fouling-release data obtained from the bacterial biofilm retraction assay based on *C. lytica*. As described by Stafslien et al. (Stafslien et al., *Biofouling*, 2007, 23(1):45-54), lower coating surface coverage by the biofilm corresponds to enhanced fouling-release performance. From Table 19, it can be seen that after preleaching coatings for 28 days all of the Example coatings which contained both SIM6492.7 and FMS-9922 displayed lower biofilm surface coverage (i.e. better fouling-release) than its corresponding Reference coatings that contained the same level of either SIM6492.7 or FMS-9922. For example, the surface coverage for Example 1 was lower than either Reference 2 or Reference 10; the surface coverage for Example 6 was lower than either Reference 7 or Reference 10; the surface coverage for Example 11 was lower than that of Reference 4 or Reference 11; and so on.

Table 20 displays *C. lytica* removal data using a water-jet pressure of 10 psi. From the data in Table 20, it can be seen that all of the Examples show higher removal than their corresponding Reference coatings.

Table 21 displays *C. lytica* removal data using a water-jet pressure of 20 psi. From the data in Table 21, it can be seen that all of the Examples show higher removal than their corresponding Reference coatings.

Table 22 displays *H. pacifica* removal data using a water-jet pressure of 15 psi. From the data in Table 22, it can be seen that all of the Examples possessing the highest level of SIM6492.7 and a FMS-9922 level of 2 or higher enabled more biofilm removal than their corresponding Reference coatings.

Table 23 displays *H. pacifica* removal data using a water-jet pressure of 25 psi. From the data in Table 23, it can be seen that all of the Examples possessing the highest level of SIM6492.7 and a FMS-9922 level of 2 or higher enabled more biofilm removal than their corresponding Reference coatings.

Table 24 displays *N. incerta* removal data using a water-jet pressure of 10 psi. From the data in Table 24, it can be seen that 13 of the 16 Examples enabled more cell removal than their corresponding Reference coatings.

Table 25 displays *N. incerta* removal data using a water-jet pressure of 20 psi. From the data in Table 25, it can be seen that 12 of the 16 Examples enabled more cell removal than their corresponding Reference coatings.

Table 26 displays barnacle removal data. From the data in Table 26, it can be seen that all of the Examples provide easier barnacle removal than their corresponding Reference coatings.

During execution of the barnacle reattachment assay, it was observed that many of the barnacles failed to attach to some of the coating surfaces. Table 27 shows the number of barnacles that failed to attach to the coating during the barnacle reattachment assay. As shown in Table 27, the Example coatings resulted in more instances of failed barnacle attachment than the reference coatings.

Table 18. Matrix used for analyzing fouling-release data.

SIM6492.7	FMS-9922 Level								
Level	0	1	2	3	4	5	6	7	8
0	Reference 1	Reference 2	Reference 3	Reference 4	Reference 5	Reference 6	Reference 7	Reference 8	Reference 9
1	Reference 10	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8
2	Reference 11	Example 9	Example 10	Example 11	Example 12	Example 13	Example 14	Example 15	Example 16

Table 19. Fouling-release data obtained from the bacterial biofilm retraction assay based on *C. lytica*. Coatings were preleached for 28 days prior to testing. All values are in percent.

SIM6492.7	FMS-9922 Level								
Level	0	1	2	3	4	5	6	7	8
0	100 ± 0	99.8 ± 0.3	99.9 ± 0.1	100 ± 0	99.8 ± 0.3	99 ± 1	88.9 ± 7.6	97.9 ± 2.9	93 ± 4.7
1	100 ± 0.1	5.4 ± 3	1.9 ± 1.3	4.2 ± 3.6	13.5 ± 23.1	0.1 ± 0.1	0.8 ± 1.1	0.5 ± 0.4	2.4 ± 1.6
2	92.7 ± 2.5	9.4 ± 9.6	1.7 ± 0.1	0.6 ± 0.6	3.2 ± 1.1	20 ± 10	9.6 ± 4.5	8.2 ± 5	13.1 ± 2.2

Table 20. *C. lytica* removal data for samples preleached for 28 days. The water-jet pressure used was 10 psi. All values are in percent.

SIM6492.7	FMS-9922 Level								
Level	0	1	2	3	4	5	6	7	8
0	35.1 ± 7.3	46.1 ± 1.9	55 ± 2.8	40.6 ± 4.7	40.3 ± 1.2	37.9 ± 5.4	41.6 ± 2.7	45.7 ± 6.9	50.9 ± 7.7
1	36.6 ± 3.1	85.6 ± 5.2	93.1 ± 1.3	95.8 ± 0.9	96.3 ± 2.8	97.1 ± 1.8	93.6 ± 6.9	93.9 ± 2.3	95.8 ± 2.8
2	30.9 ± 1.9	94.8 ± 2	96 ± 0	96.7 ± 0.7	95.9 ± 0.4	94.7 ± 2	92.3 ± 5.3	97.3 ± 0.3	99.6 ± 0.2

Table 21. *C. lytica* removal data for samples preleached for 28 days. The water-jet pressure used was 20 psi. All values are in percent.

SIM6492.7	FMS-9922 Level								
Level	0	1	2	3	4	5	6	7	8
0	48.1 ± 3.8	53.2 ± 1	67.1 ± 4.2	56.4 ± 3.6	52.6 ± 3.1	54.8 ± 1.5	54.3 ± 6.9	63.7 ± 0.8	67.4 ± 5.5
1	42.2 ± 11.5	91.6 ± 3.2	97.3 ± 1	97.3 ± 0.8	99.8 ± 1.4	98.5 ± 0.7	94.3 ± 8.4	94.6 ± 3.6	98 ± 0.6
2	42.5 ± 1.4	97.8 ± 0.7	96.1 ± 3.1	99.1 ± 0.5	99 ± 0.4	97.2 ± 2.1	96.8 ± 2.4	97 ± 0.6	100 ± 0.3

Table 22. *H. pacifica* removal data for samples preleached for 28 days. The water-jet pressure used was 15 psi. All values are in percent.

SIM6492.7	FMS-9922 Level								
Level	0	1	2	3	4	5	6	7	8
0	15.6 ± 6.7	4.8 ± 3.6	27.3 ± 5.9	4.6 ± 8.2	12.4 ± 5.7	21.9 ± 9	11.9 ± 3.1	12.1 ± 5.8	31.6 ± 6
1	15.2 ± 2.5	15 ± 2.1	0 ± 14.3	25 ± 7.2	14.4 ± 7	21.4 ± 5.2	24.6 ± 5.2	72.5 ± 0.5	48.4 ± 6.7
2	0 ± 26.8	2.1 ± 6.9	37.1 ± 8.5	8.5 ± 2.8	50 ± 1.8	28.4 ± 15.7	57.4 ± 2.5	87.6 ± 19	80.9 ± 5.5

Table 23. *H. pacifica* removal data for samples preleached for 28 days. The water-jet pressure used was 25 psi. All values are in percent.

SIM6492.7	FMS-9922 Level								
Level	0	1	2	3	4	5	6	7	8
0	6.6 ± 6.7	5.2 ± 3.9	20.9 ± 9.9	0 ± 15.5	23.3 ± 5.6	30.8 ± 10.8	15.3 ± 6.7	9.2 ± 4.5	52.4 ± 3.1
1	26.1 ± 5.7	16.1 ± 6.3	0 ± 14.3	33.1 ± 2.1	15.8 ± 8.1	41.5 ± 15.7	29.4 ± 3.4	84.8 ± 1.5	49.6 ± 4.9
2	0 ± 26.8	0 ± 7.7	27.3 ± 7.2	16.3 ± 3.5	52.5 ± 6.3	59.9 ± 12.4	63.9 ± 4.2	98.4 ± 3.6	100 ± 8.3

Table 24. *N. incerta* removal data for samples preleached for 28 days. The water-jet pressure used was 10 psi. All values are in percent.

SIM6492.7	FMS-9922 Level								
Level	0	1	2	3	4	5	6	7	8
0	25 ± 12.5	4.7 ± 2.5	12.4 ± 2.2	17.4 ± 16	13.3 ± 0.3	18.4 ± 1.5	19.9 ± 3.2	12.2 ± 2.9	21.7 ± 3.3
1	8.9 ± 1.5	24.5 ± 1.6	33.7 ± 23.8	22.2 ± 4	20 ± 19.9	25.1 ± 11.3	25.1 ± 15.3	17.1 ± 6.6	23.2 ± 5.7
2	14.3 ± 2.3	23.7 ± 2.4	17 ± 4.3	18.2 ± 11.6	15.2 ± 4	16.2 ± 4.9	13.1 ± 9.2	23.3 ± 6.5	29.9 ± 2.6

Table 25. *N. incerta* removal data for samples preleached for 28 days. The water-jet pressure used was 20 psi. All values are in percent.

SIM6492.7	FMS-9922 Level								
Level	0	1	2	3	4	5	6	7	8
0	39.3 ± 5.5	29.3 ± 3.7	32.1 ± 1	33.2 ± 4.1	38.3 ± 5.4	39.3 ± 7.7	35.4 ± 2	35.8 ± 2.6	39.2 ± 3.3
1	31.3 ± 2.6	39.2 ± 7.9	54.1 ± 11.2	43 ± 5.5	39.9 ± 15.5	33.4 ± 6.6	37.9 ± 11.5	36.2 ± 6	52.4 ± 3.3
2	34.1 ± 5.4	44.4 ± 6.5	37.5 ± 8.4	39 ± 10.7	41.6 ± 3	47.3 ± 0.7	47.7 ± 10.7	51.2 ± 2.9	49.6 ± 3.1

Table 26. Fouling-release data obtained using the barnacle reattachment assay. Coatings were preleached for 28 days prior to testing. All values are in MPa.

SIM6492.7	FMS-9922 Level								
Level	0	1	2	3	4	5	6	7	8
0	0.23 ± 0.03	0.18 ± 0.04	0.16 ± 0.03	0.16 ± 0.03	0.18 ± 0.02	0.15 ± 0.02	0.13 ± 0.07	0.15 ± 0.03	0.15 ± 0.05
1	0.13 ± 0.03	0.13 ± 0.03	0.1 ± 0.04	0.11 ± 0.04	0.13 ± 0.02	0.08 ± 0.05	0.07 ± 0.03	0.1 ± 0.02	0.08 ± 0.02
2	0.15 ± 0.04	0.11 ± 0.03	0.08 ± 0.04	0.09 ± 0.04	0.08 ± 0.04	0.09 ± 0.01	0.17 *	0.08 ± 0.03	0.05 ± 0.02

* Only one measurement was acquired due to inability of barnacles to attach to these surfaces

Table 27. Number of barnacles that failed to attach to the coating during the barnacle reattachment assay. Coatings were preleached for 28 days prior to testing. All values are number of non-attached barnacles out of nine total.

SIM6492.7	FMS-9922 Level								
Level	0	1	2	3	4	5	6	7	8
0	1	0	0	0	0	0	0	1	3
1	0	2	1	2	3	3	2	5	6
2	1	0	3	3	3	7	8	7	5

Figure 1 displays the general compositional space that is being investigated for the production of novel fouling-release coatings based the generation of amphiphilic surfaces. Figure 2 shows fouling release data as a function of both CF_3-PDMS and TMS-PEG content. The fouling-release rating is the average rank obtained for 20 different coatings characterized using 4 different fouling-release measurements each based on a different organism. Thus, the lower the fouling-release rating, the better the overall fouling-release performance. As shown in Figure 2, initial laboratory experiments showed a synergist effect between the silanol-terminated, fluorine-containing siloxane (CF_3-PDMS) and the trimethoxysilane-functional PEG (TMS-PEG) on fouling-release properties. As a result, a follow-up experiment was conducted that focused on higher levels of CF_3-PDMS and two levels of TMS-PEG.

Figures 3 and 4 exhibit fouling-release data obtained using two different marine bacteria, namely, *C. lytica* and *H. pacifica*, respectively. For *C. lytica* (Figure 3), a dramatic synergy between the presence of CF_3-PDMS and TMS-PEG can be easily seen. For example, without the presence of CF_3-PDMS, there was essentially no significant difference in biofilm retention, biofilm retraction, and biofilm removal as a function of TMS-PEG content. However, replacement of just 10 weight percent of the silanol terminated PDMS with CF_3-PDMS in coatings containing TMS-PEG resulted in a dramatic reduction in biofilm retention and biofilm surface coverage and a major increase in biofilm removal.

For *H. pacifica* (Figure 4), the addition of TMS-PEG to PDMS-based coatings (i.e. no CF_3-PDMS) resulted in a significant reduction in biofilm retention. Partial substitution of silanol-terminated PDMS with CF_3-PDMS resulted in a further decrease in biofilm retention with increasing CF_3-PDMS content.

With regard to biofilm removal, a dramatic increase in biofilm removal was achieved by increasing CF_3-PDMS content in coatings containing PEG modification. For example, the coating based on 8 wt. % TMS-PEG and no CF_3-PDMS showed no biofilm removal at a pressure of 20 psi; however, when 30 wt. % of the silanol-terminated PDMS was replaced by CF_3-PDMS in this composition, complete removal of the biofilm was obtained.

Figure 5 exhibits data obtained the marine algae, *N. incerta.* For this microorganism, cell attachment exhibited a minimum at compositions possessing the low level of TMS-PEG (i.e. 6 wt. %) a CF_3-PDMS content of 17 wt. % based on total siloxane. With regard to removal, all the coatings exhibited very similar performance.

Barnacle adhesion strength was assessed using the barnacle reattachment assay. As shown in Figure 6 and determined using statistical analysis, the incorporation of PEG moieties as well as CF_3-PDMS decreased barnacle adhesion strength. In addition, a synergist interaction between TMS-PEG and CF_3-PDMS was observed. As shown in Figure 6 (right), a correlation was observed between the number of barnacles that would not attach and coating composition. For the assay, 10 barnacles were used for assessing adhesion strength. As shown in Figure 6 (right), coatings possessing relatively high levels of CF_3-PDMS and TMS-PEG inhibited barnacle attachment. In addition, as illustrated in Figure 7, barnacles removed from the coatings possessing relatively high levels of CF_3-PDMS and TMS-PEG showed “cupped” or “domed” base-plate morphology that was not observed for barnacles attached to the pure PDMS-based coating or a commercial fouling-release coating (Intersleek 970).

To illustrate the overall fouling-release performance of the coatings, the coatings were ranked from 1 to 27, with 1 being the best performing coating and 27 being the worst, for each fouling-release measurement made. For each coating, the rank values were averaged and are plotted in Figure 8. From figure 8, the synergist interaction between TMS-PEG and CF_3-PDMS on fouling-release properties can be very easily observed.

In addition to the experimental coatings, the commercial fouling-release coating, Intersleek 970, was included in the experiment. Figure 9 provides a comparison of the experimental coating derived from the highest TMS-PEG and CF_3-PDMS content to Intersleek 970. The spider plot shown in Figure 9 was generated by normalizing all the data so that the value pertaining to the best performing coating of the two would be given the value of 1.0 and the value of the other coating would be expressed as a fraction of the value of the former. In addition, reattached barnacle adhesion was inversely transformed (1/value) so that higher values indicate lower adhesion strength. By expressing the data in this fashion, a larger area enclosed within the spider plot indicates better overall fouling release performance. From Figure 9, it can be seen that the experimental coating was similar in performance to IS 970 with regard to bacterial biofilm removal and barnacle removal, but significantly better with respect to diatom removal.

Example III

Polysiloxane Coatings Containing Fluorinated Siloxane Segments

Amphiphilicity can be incorporated into polysiloxanes using both commercially-available starting materials as well as synthetically produced polysiloxane oligomers. Figures 10 to 12 display the synthetic schemes that can be carried out. The synthetic schemes shown in Figures 10 and 11 are completely based on commercially-available starting materials, while the synthetic scheme shown in Figure 12 requires both monomer synthesis and ring-opening polymerization to produce oligomers for coating preparation.

Figure 10 shows an illustrative synthetic scheme for generating amphiphilic polysiloxane coatings using commercially available starting materials and an addition-cure mechanism. The vinyl and hydride functionalities can be on any of the starting materials; only one representative reaction is shown.

Figure 11 shows a synthetic scheme for generating amphiphilic polysiloxane coatings using commercially available starting materials and a moisture-cure mechanism. Hydrophilic groups are incorporated via the trimethoxysilane crosslinker.

Figure 12 shows a synthetic scheme for generating amphiphilic polysiloxane coatings using hydrosilylation reaction to generate a functionalized cyclic siloxane, an anionic ring-opening mini-emulsion polymerization to produce novel silanol-terminated amphiphilic polysiloxanes, and production of coatings using the silanol-erminated amphiphilic polysiloxanes using a moisture-cure mechanism.

It should be understood that any and all features of the invention recited herein, including but not limited to various individual components of the polymer reaction mixture, various parameters concerning structure, methods of use, and the like, whether or not said components or features are recited together in the context of one embodiment or recited in different passages herein with respect to different embodiments, can be combined together in any combination to form the novel compositions or methods as envisioned by the invention.

Moreover, the complete disclosures of all patents, patent applications including provisional patent applications, and publications, and electronically available material cited herein are incorporated by reference. The foregoing detailed description and examples have been provided for clarity of understanding only. No unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described; many variations will be apparent to one skilled in the art and are intended to be included within the invention defined by the claims.

What is claimed is:

1. A polymeric material formed by reacting a mixture comprising at least one hydrophilic component, at least one fluorine-containing component, and at least one silanol-terminated polysiloxane.

2. A substrate comprising a surface comprising an fouling-release coating, wherein the coating comprises a polymeric material formed by reacting a mixture comprising a hydrophilic component, a fluorine-containing component, and silanol-terminated polysiloxane.

3. A maritime vessel comprising a polymeric coating comprising a polymeric material formed by reacting a mixture comprising a hydrophilic component, a fluorine-containing component, and silanol-terminated polysiloxane.

4. The polymeric material, substrate or vessel of any of the preceding claims wherein the hydrophilic component comprises a silane-functional hydrophilic component.

5. The polymeric material, substrate or vessel of any of the preceding claims wherein the hydrophilic component comprises a polyalkyleneglycol.

6. The polymeric material, substrate or vessel of any of the preceding claims wherein the fluorine-containing component is a silane-functional fluorine-containing compound.

7. The polymeric material, substrate or vessel of claim 4 or 6 wherein the silane-functional compound comprises an alkoxysilane.

8. The polymeric material, substrate or vessel of any of the preceding claims wherein at least one of the fluorine-containing component and the hydrophilic component comprises a polymer.

9. The polymeric material, substrate or vessel of any of the preceding claims wherein at least one of the fluorine-containing component and the hydrophilic component comprises a silanol-terminated polysiloxane.

10. The polymeric material, substrate or vessel of any of the preceding claims wherein the silanol-terminated polysiloxane comprises a homopolymer.

11. The polymeric material, substrate or vessel of any of the preceding claims wherein the silanol-terminated polysiloxane comprises a heteropolymer

12. The polymeric material, substrate or vessel of any of the preceding claims wherein the silanol-terminated polysiloxane comprises a copolymer.

13. The polymeric material, substrate or vessel of claim 12 wherein the copolymer comprises a block copolymer or random copolymer.

14. The polymeric material, substrate or vessel of any of the preceding claims wherein the silanol-terminated polysiloxane comprises at least one of the fluorine-containing component and the hydrophilic component.

15. The polymeric material, substrate or vessel of claim 14 wherein the polysiloxane comprises a copolymer.

16. The polymeric material, substrate or vessel of any of the preceding claims wherein the silanol-terminated polysiloxane comprises silanol-terminated polydimethylsiloxane.

17. The polymeric material of any of the preceding claims which does not comprise silicone oil.

18. A method for making the polymeric material of any of the preceding claims comprising reacting at least one hydrophilic component, at least one fluorine-containing

component, and at least one silanol-terminated polysiloxane under conditions to yield a polymeric material.

19. The method of claim 18 further comprising reacting a crosslinking agent with the at least one hydrophilic component, at least one fluorine-containing component, and at least one silanol-terminated polysiloxane.

20. A method for making a polymeric material comprising reacting at least one vinyl functionalized first component, at least one hydride functionalized second component, and a silanol-terminated polysiloxane, wherein at least one of the first and second components comprises a hydrophilic group and at least one of the first and second components comprises a fluorine-containing group, under conditions to yield a polymeric material.

21. A method for making a functionalized siloxane comprising reacting at least one vinyl functionalized first component, at least one hydride functionalized second component, and a vinyl- or hydride-functionalized polysiloxane, wherein at least one of the first and second components comprises a hydrophilic group and at least one of the first and second components comprises a fluorine-containing group, under conditions to yield a functionalized siloxane.

22. The method of claim 22 wherein the functionalized siloxane is a cyclic siloxane.

23. A method for making a silanol-terminated polysiloxane comprising subjecting the functionalized siloxane produced by the method of claim 21 or 22 to anionic ring-opening miniemulsion polymerization under conditions to yield a silanol-terminated polysiloxane.

24. The method of claim 23 wherein the silanol-terminated polysiloxane comprises an amphiphilic copolymer comprising at least one hydrophilic group at least one fluorine-containing group.

25. A polymeric material formed by reacting the amphiphilic silanol-terminated polysiloxane produced by the method of claim 24 with polydimethylsiloxane.

26. A method of protecting the surface of a substrate comprising coating the substrate surface with the polymeric material of any of claims 1 to 17.

27. A method of facilitating the removal of a biofilm or marine organism from a substrate surface comprising coating the surface with a polymeric material of any of claims 1 to 17.

Figure 1

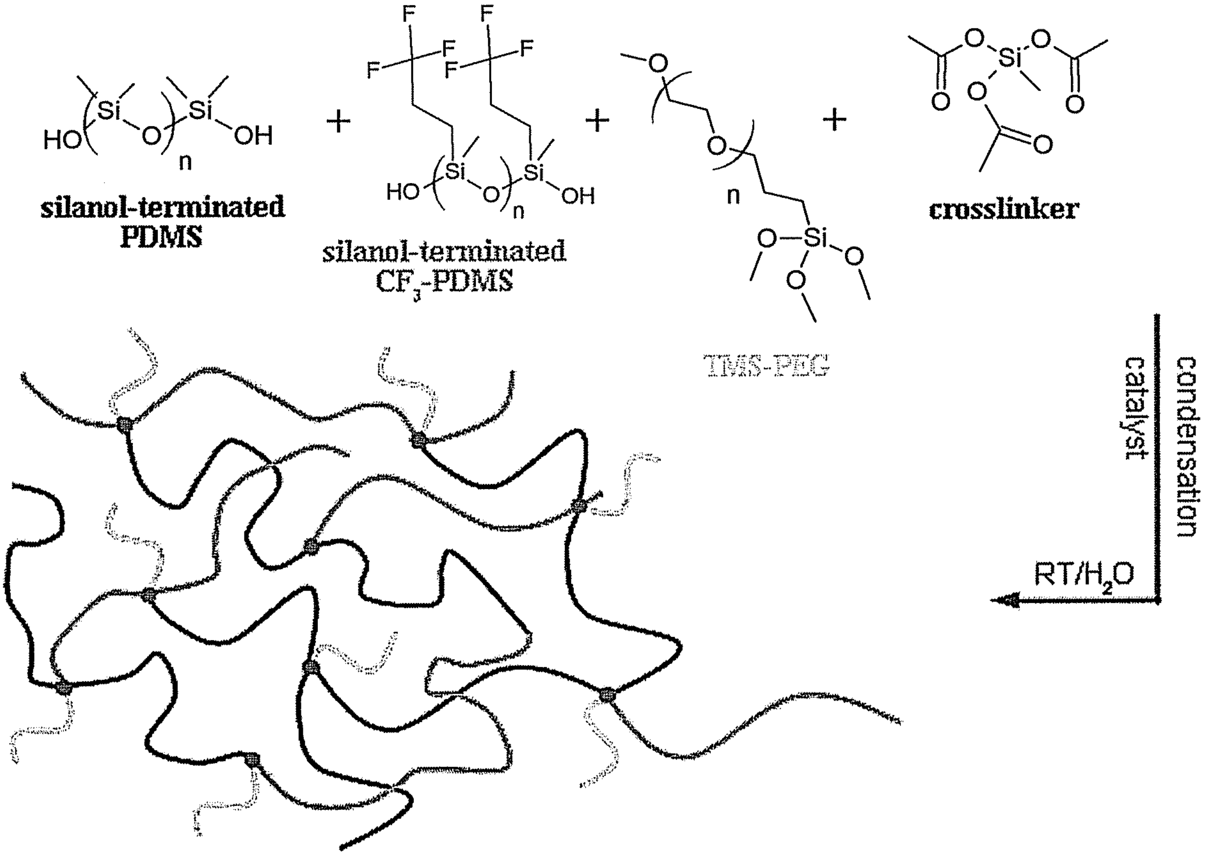

HO
Si
O
Si
OH
n
silanol-terminated PDMS
F
F
F
Si
O
Si
OH
HO
n
silanol-terminated CF$_3$-PDMS
O
O
n
O
Si
O
O
TMS-PEG
O
Si
O
O
O
O
O
crosslinker
+
condensation catalyst
RT/H$_2$O

Figure 2

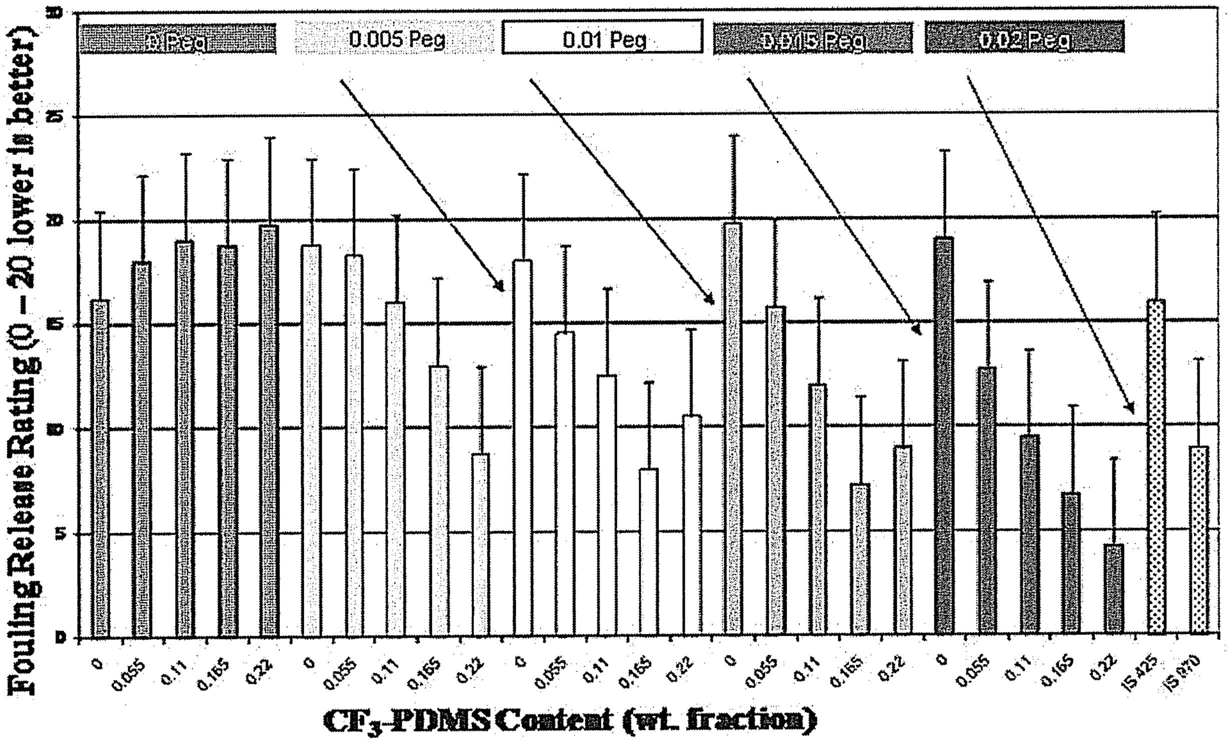

0 Peg
0.005 Peg
0.01 Peg
0.015 Peg
0.02 Peg
Fouling Release Rating (0 – 20 lower is better)
0
5
10
15
20
25
30
0
0.055
0.11
0.165
0.22
0
0.055
0.11
0.165
0.22
0
0.055
0.11
0.165
0.22
0
0.055
0.11
0.165
0.22
0
0.055
0.11
0.165
0.22
IS 425
IS 970
CF$_3$-PDMS Content (wt. fraction)

Figure 3

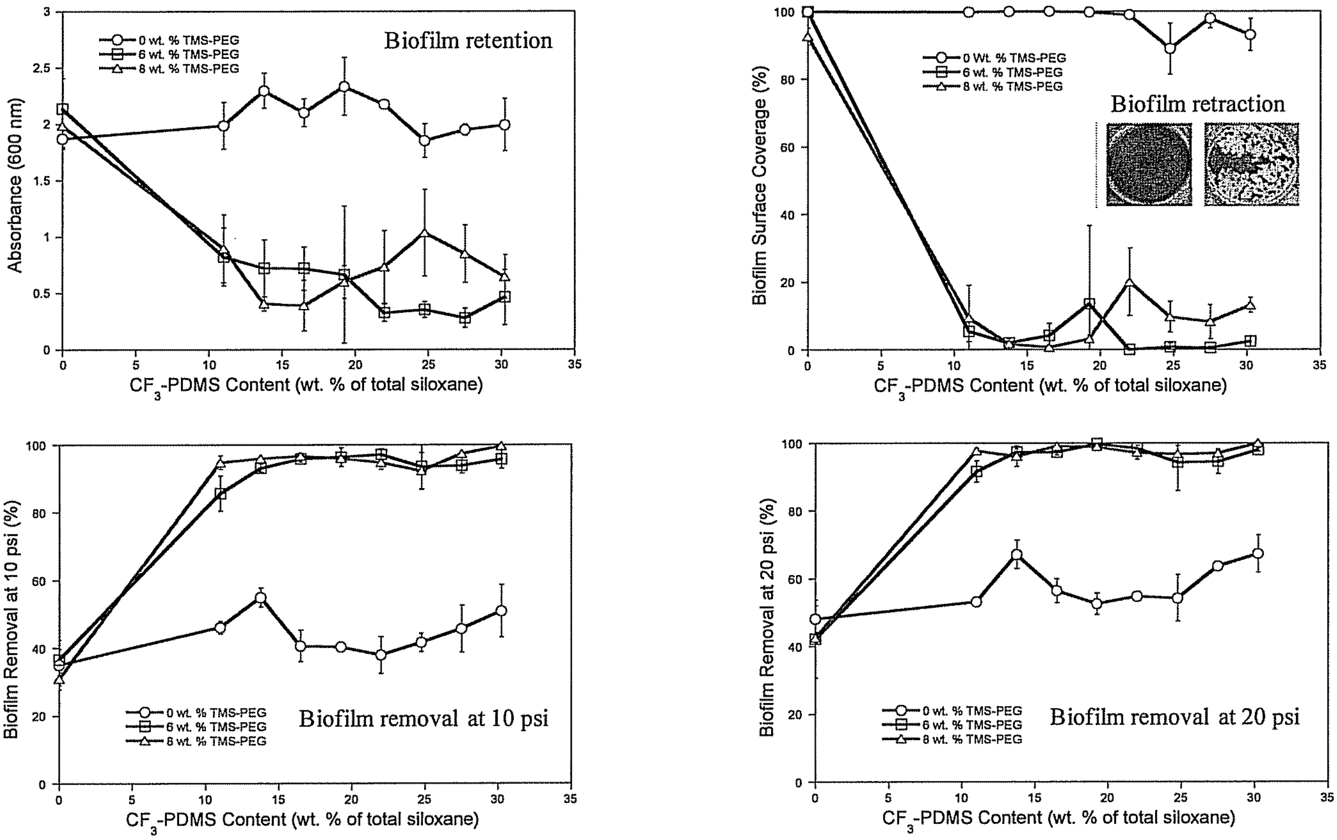

Biofilm retention
Absorbance (600 nm)
0 wt. % TMS-PEG
6 wt. % TMS-PEG
8 wt. % TMS-PEG
CF$_3$-PDMS Content (wt. % of total siloxane)
0
0.5
1
1.5
2
2.5
3
5
10
15
20
25
30
35
Biofilm retraction
Biofilm Surface Coverage (%)
0 Wt. % TMS-PEG
6 wt. % TMS-PEG
8 wt. % TMS-PEG
20
40
60
80
100
Biofilm removal at 10 psi
Biofilm Removal at 10 psi (%)
Biofilm removal at 20 psi
Biofilm Removal at 20 psi (%)

Figure 4

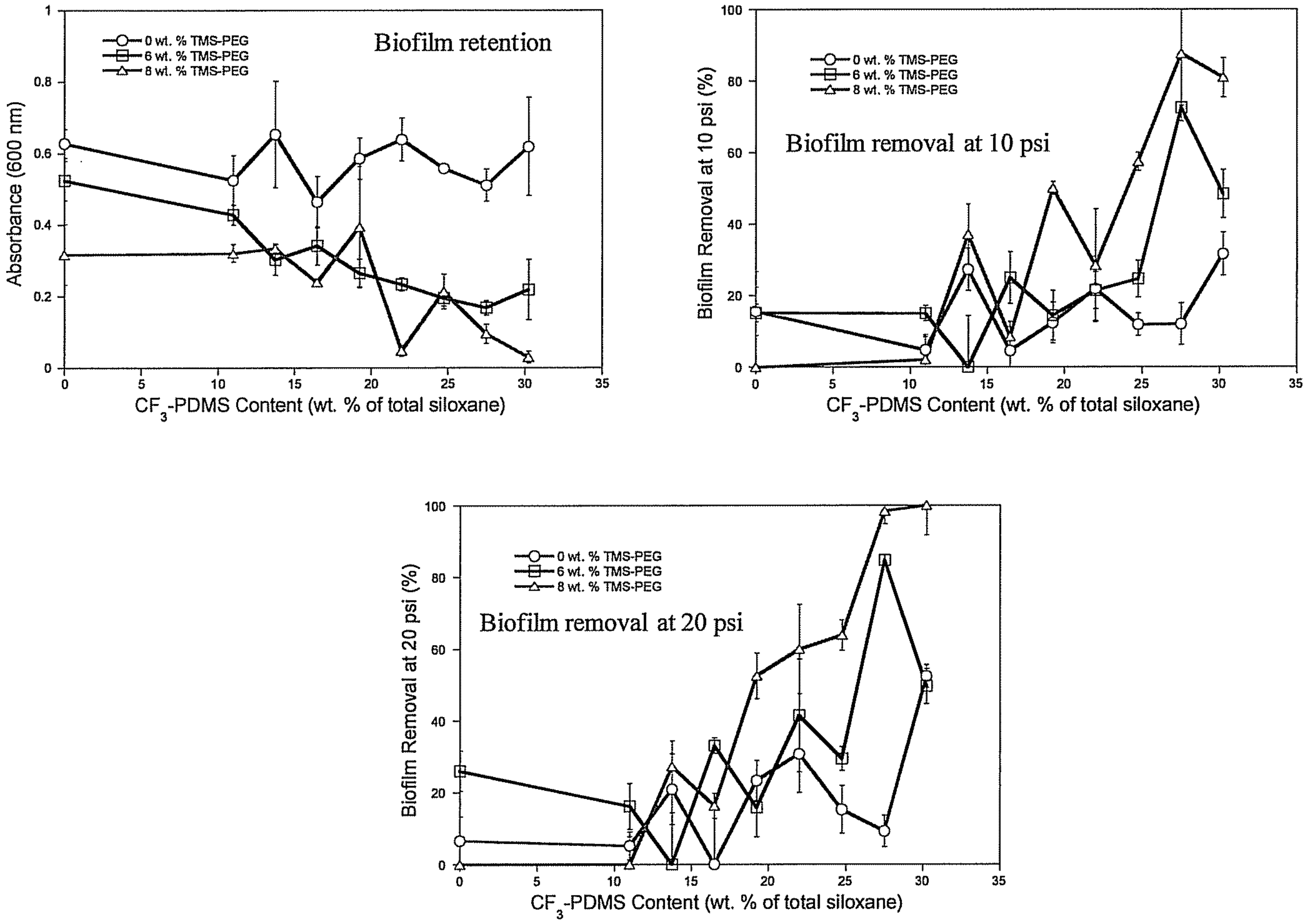

Biofilm retention
0 wt. % TMS-PEG
6 wt. % TMS-PEG
8 wt. % TMS-PEG
Absorbance (600 nm)
1
0.8
0.6
0.4
0.2
0
0 5 10 15 20 25 30 35
CF$_3$-PDMS Content (wt. % of total siloxane)
Biofilm removal at 10 psi
0 wt. % TMS-PEG
6 wt. % TMS-PEG
8 wt. % TMS-PEG
Biofilm Removal at 10 psi (%)
100
80
60
40
20
0
0 5 10 15 20 25 30 35
CF$_3$-PDMS Content (wt. % of total siloxane)
Biofilm removal at 20 psi
0 wt. % TMS-PEG
6 wt. % TMS-PEG
8 wt. % TMS-PEG
Biofilm Removal at 20 psi (%)
100
80
60
40
20
0
0 5 10 15 20 25 30 35
CF$_3$-PDMS Content (wt. % of total siloxane)

Figure 5

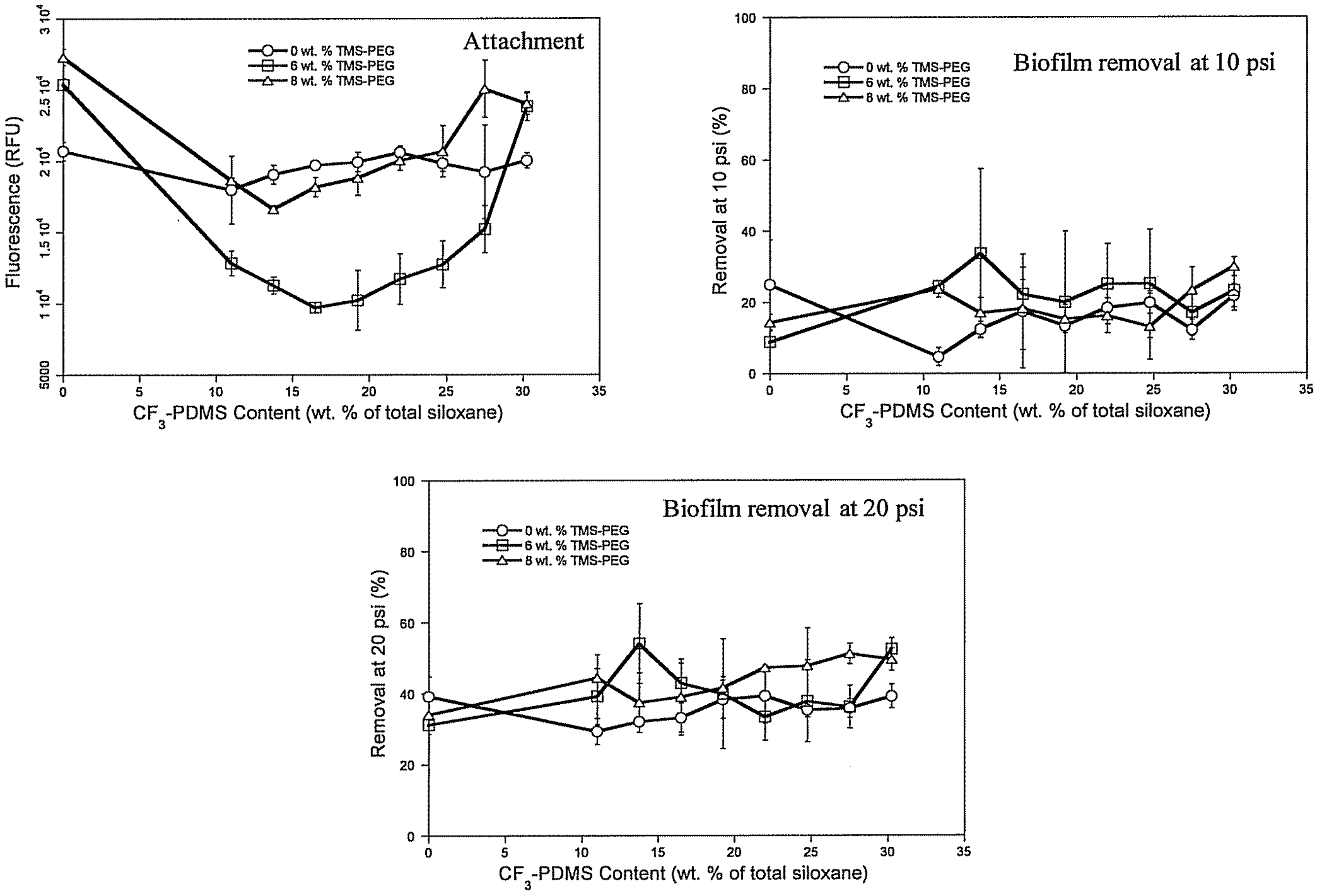


Figure 6

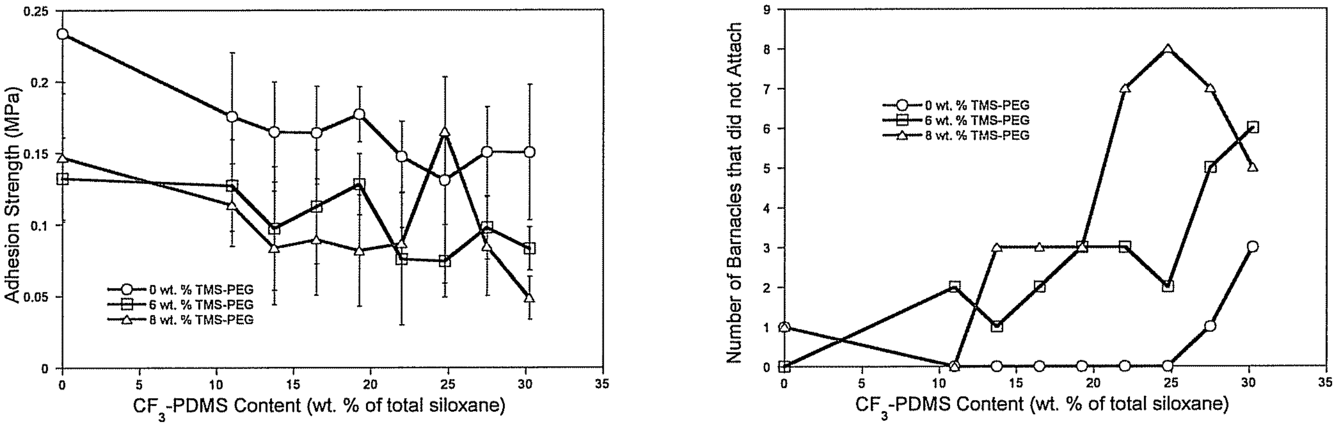
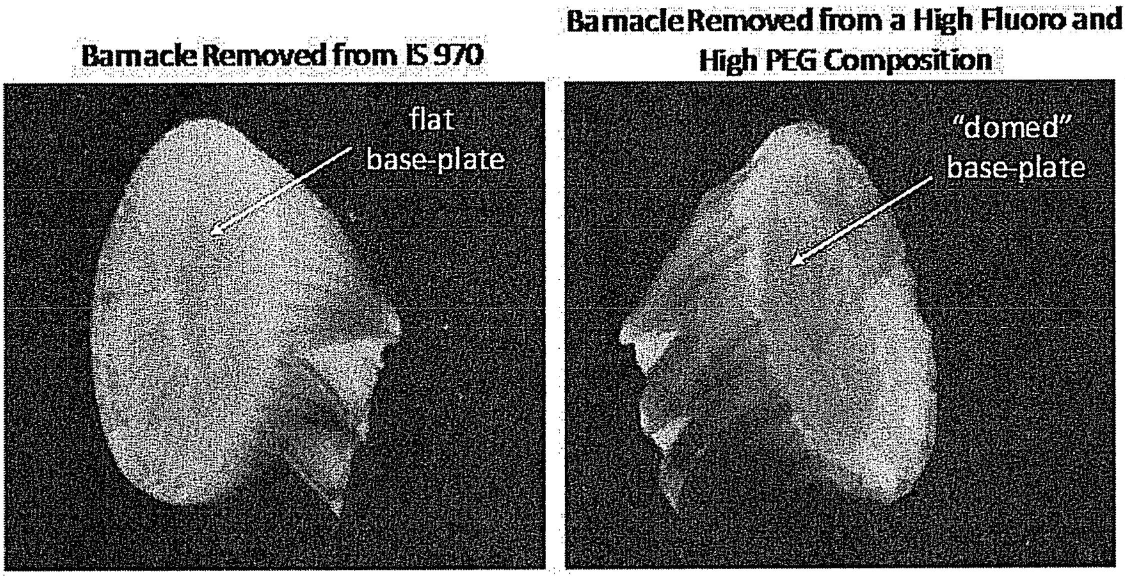


Figure 7



Barnacle Removed from IS 970

Barnacle Removed from a High Fluoro and High PEG Composition

Figure 8

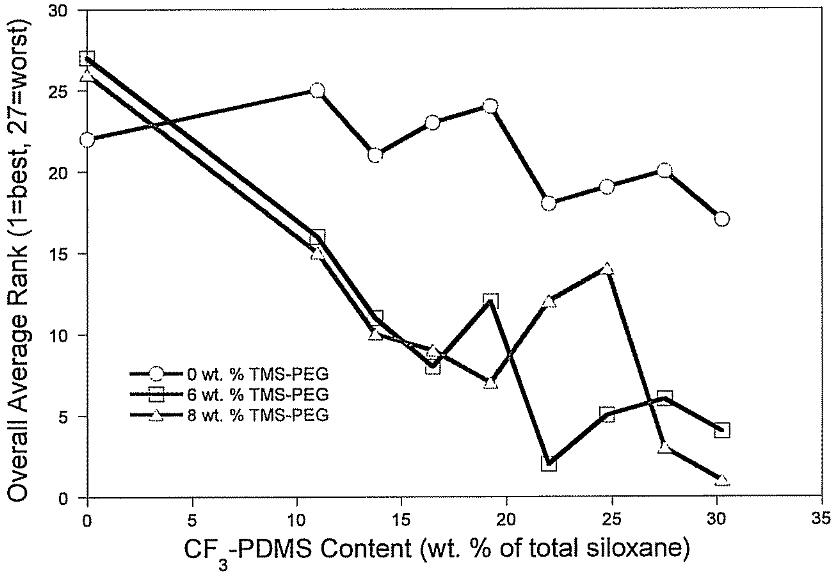
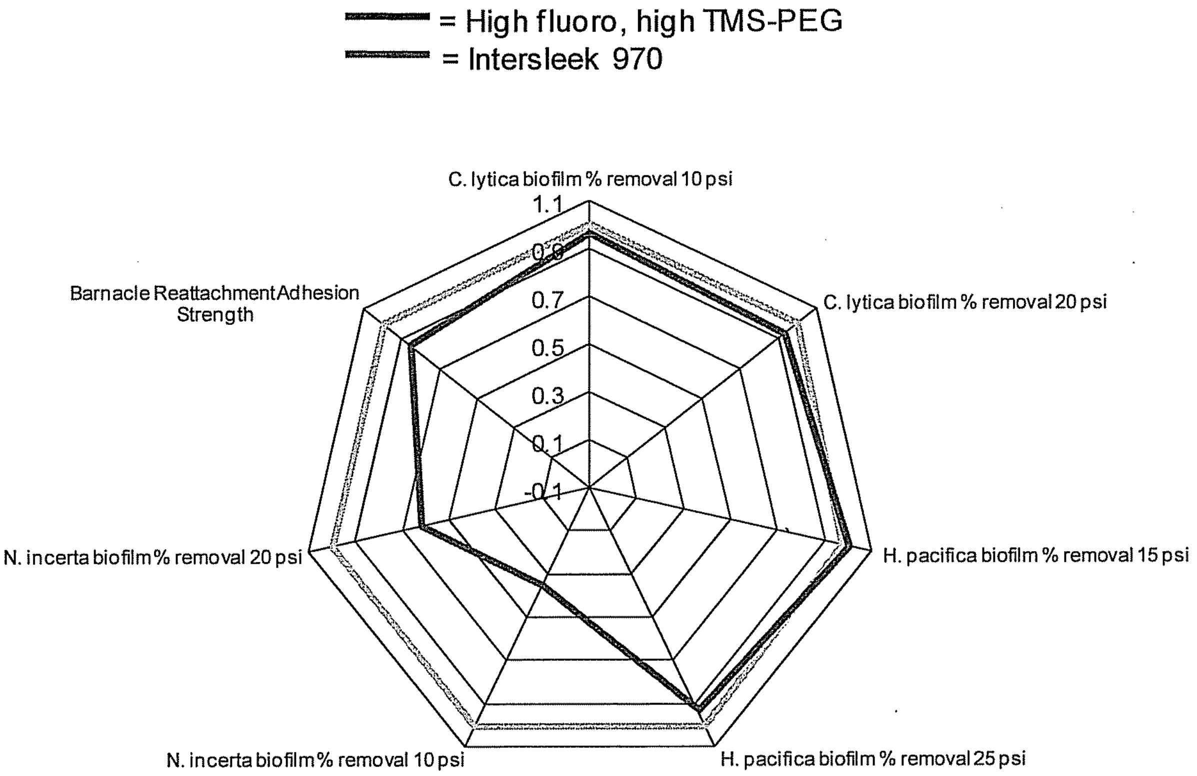


Figure 9



Note: Data was normalized from 0=worse to 1=best to compare all assays side by side. Barnacle Reattachment data was inverse transformed (1/value) prior to normalization

Figure 10

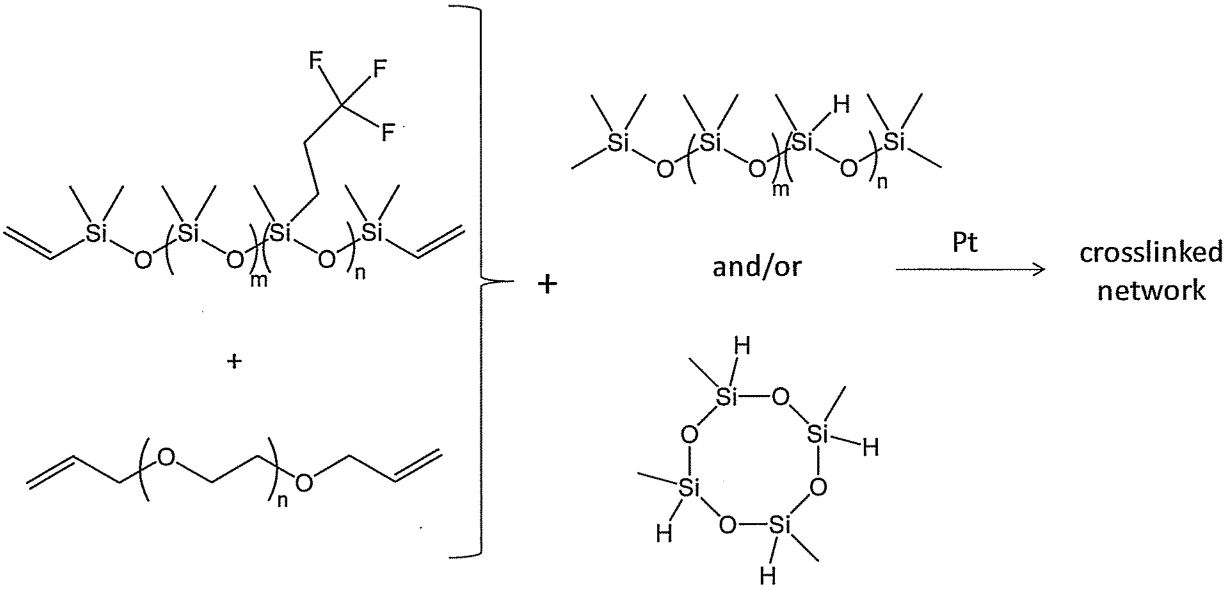


Figure 11

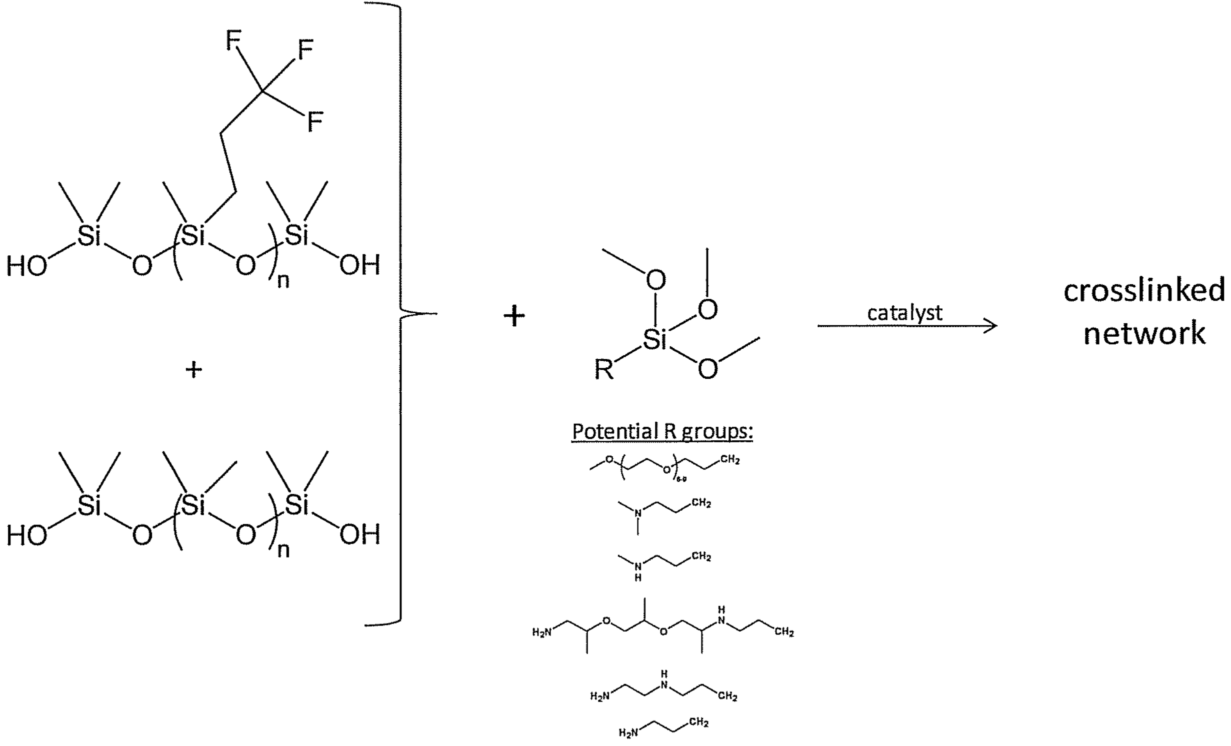
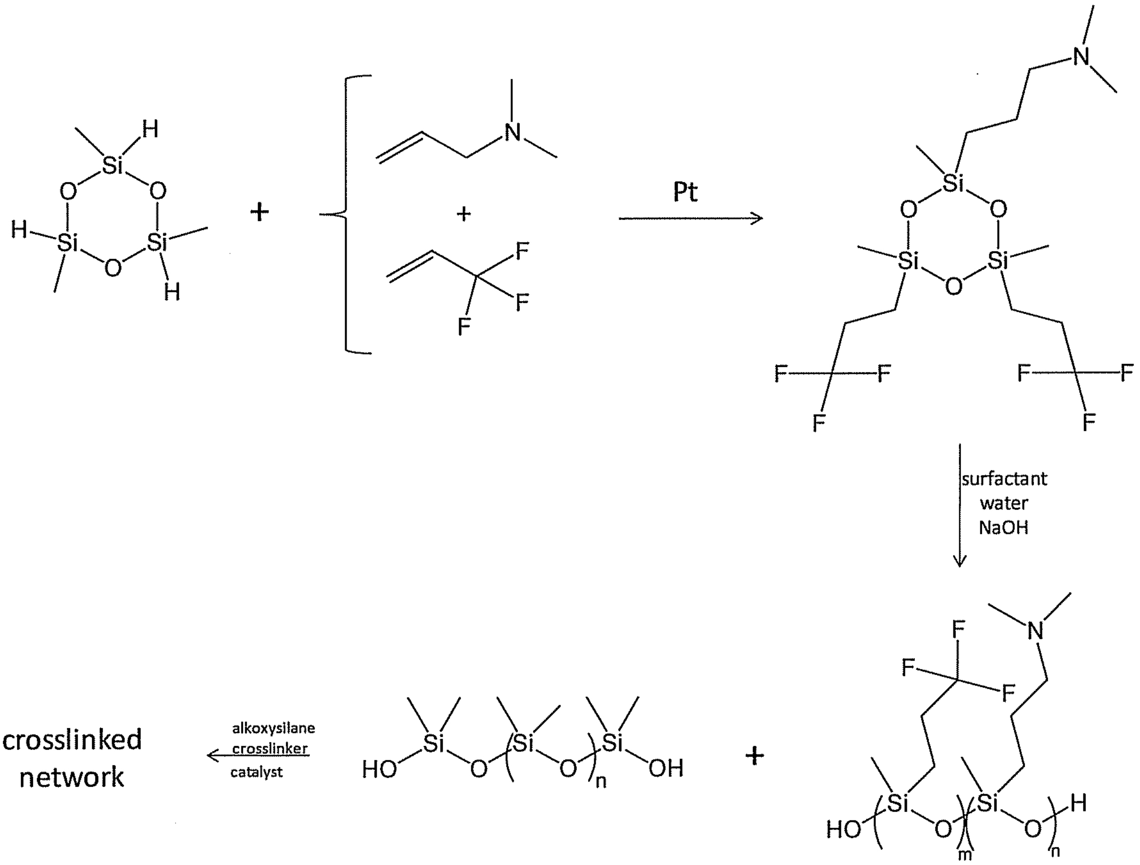


Figure 12


Pt
surfactant
water
NaOH
alkoxysilane
crosslinker
catalyst
crosslinked
network
Si
O
H
N
F
HO
OH
n
m

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 10/58968

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C08L 27/12; A01N 55/10; C08G 77/14; C08G 77/12 (2011.01)
USPC - 525/104; 524/588; 525/474
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
USPC - 525/104; 524/588; 525/474
IPC(8) - C08L 27/12; A01N 55/10; C08G 77/14; C08G 77/12 (2011.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 525/104; 524/588; 525/474 (keyword delimited)
IPC(8) - C08L 27/12; A01N 55/10; C08G 77/14; C08G 77/12 (2011.01)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWEST (USPT,PGPB,EPAB,JPAB); Google
Search terms used: fouling biocide silane siloxane hydrophilic coat marine vessel

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2009/0221752 A1 (Dahling et al.) 03 September 2009 (03.09.2009), para [0014], [0002], [0035]	1-4
Y	US 2006/0194764 A1 (Kim) 31 August 2006 (31.08.2006), para [0003], [0075], [0038], [0010]	1-4
Y	US 2009/0094954 A1 (Nakayama et al.) 16 April 2009 (16.04.2009), para [0017]-[0020], [0052]	1-4

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search
06 April 2011 (06.04.2011)

Date of mailing of the international search report
19 APR 2011

Name and mailing address of the ISA/US
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450
Facsimile No. 571-273-3201

Authorized officer:
Lee W. Young
PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 10/58968

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 5-19, 26, 27
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
Claim groups found:
Group I: Claims 1-4
Group II: Claims 20-25

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

-- see extra sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-4

Remark on Protest
☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
☐ No protest accompanied the payment of additional search fees.

Continuation of Box No. III -- Observations where unity of invention is lacking

Group I: is directed to a polymeric material formed by reacting a mixture comprising at least one hydrophilic component, at least one fluorine-containing component, and at least one silanol-terminated polysiloxane.

Group II: is directed to a method for making a functionalized siloxane comprising reacting at least one vinyl functionalized first component, at least one hydride functionalized second component, and a silanol-terminated polysiloxane, wherein at least one of the first and second components comprises a hydrophilic group and at least one of the first and second components comprises a fluorine-containing group, under conditions to yield a polymeric material.

The inventions listed as Groups I-II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Groups I and II lack unity of invention, because even though the inventions of these groups require the technical features of a component comprising a hydrophilic group, a component comprising a fluorine-containing group and a silanol-terminated polysiloxane, these technical features are not special technical features as they do not make a contribution over the prior art in view of US 2009/0221752 A1 to Dahling et al., which discloses an anti-fouling composition (title) comprising a functionalized siloxane (para [0065], [0014], monomer B), a component comprising a hydrophilic group (para [0014], monomer C - silane) and a component comprising a fluorine-containing group (para [0014], monomer A) and, further, US 2006/0194764 A1 to Kim et al. which discloses an aniti-fouling composition (para [0056]) comprising a silanol-functionalized siloxane (para [0003], [0075], [0038]). It would have been obvious to one of skill in the art to use the silanol functionalized siloxane, as disclosed by Kim, in the antifouling composition, as disclosed by Dahling, wherein silanol containing molecules have been found to be powerful antimicrobial agents, and are generally environmentally friendly and affordable agents (see Kim para [0010]).

Groups I-II therefore lack unity under PCT Rule 13 because they do not share a same or corresponding special technical feature.