SUMMARY

~~In an aspect,~~There is provided a method for establishing a fouling-release coating system on a surface of a substrate is provided, which comprises the sequential steps of;

a. optionally applying one or more layers of a primer composition onto the surface of said substrate and allowing said layer(s) to cure, thereby forming a primed substrate;

b. applying one or more layers of silicone-containing tie-coat composition in liquid form, onto the surface of said primed substrate or said substrate, and allowing said layer(s) to cure, thereby forming a cured tie-coat layer;

c. applying one or more layers of a fouling-release coating composition onto said cured tie–coat layer, wherein said fouling-release coating composition comprises a condensation-curable polysiloxane-based binder matrix constituting at least 40 % by dry weight of said coating composition, wherein more than 65 % by weight of said binder matrix is represented by polysiloxane parts, and allowing said fouling-release coating composition to cure;

wherein said tie-coat composition and/or said fouling-release coating composition comprises constituents having poly(oxyalkylene) chains,

and wherein said tie-coat composition and/or said fouling-release coating composition further comprises one or more sterically hindered amines, in particular 2,2,6,6-tetraalkyl piperidine derivatives.

~~In another aspect,~~There is also provided a fouling-release coating system obtained by this method as defined above is also provided. In another aspect, a fouling-release coating system is also provided which comprises:

a. a substrate,
b. optionally one or more primer layers,
c. at least one silicone-containing tie-coat layer
d. a fouling-release layer comprising a condensation-cured polysiloxane-based binder matrix constituting at least 40 % by dry weight of said coat, wherein more than 65 % by weight of said binder matrix is represented by polysiloxane parts, said coat comprising constituents having poly(oxyalkylene) chains,

wherein said tie-coat layer and/or said fouling-release layer further comprises one or more sterically hindered amines, in particular 2,2,6,6-tetraalkyl piperidine derivatives.

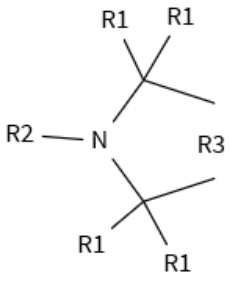
In an aspect, there is provide a method for establishing a fouling-release coating system on a surface of a substrate comprising the sequential steps of;

a. optionally applying one or more layers of a primer composition onto the surface of said substrate and allowing said layer(s) to cure, thereby forming a primed substrate;

b. applying one or more layers of silicone-containing tie-coat composition in liquid form, onto the surface of said primed substrate or said substrate, and allowing said layer(s) to cure, thereby forming a cured tie-coat layer;

c. applying one or more layers of a fouling-release coating composition onto said cured tie–coat layer, wherein said fouling-release coating composition comprises a condensation-curable polysiloxane-based binder matrix constituting at least 40 % by dry weight of said coating composition, wherein more than 65 % by weight of said binder matrix is represented by polysiloxane parts, and allowing said fouling-release coating composition to cure; wherein said tie-coat composition and/or said fouling-release coating composition comprises constituents having poly(oxyalkylene) chains, and wherein said tie-coat composition and/or said fouling-release coating composition further comprises one or more sterically hindered amines,

wherein the sterically hindered amines are hindered amine moieties of the general formula I:



wherein

each R1 is independently linear or branched C_1-C_4 alkyl;

R2 is selected from -H, optionally substituted linear or branched C_{1-30}-alkyl, optionally substituted linear or branched C_{2-30}-alkenyl, optionally substituted aryl, -OH, optionally substituted linear or branched C_{1-30}-alkoxy, optionally substituted linear or branched C_{1-30}-alkenyloxy, optionally substituted aryloxy, optionally substituted linear or branched C_{1-30}-alkylcarbonyl, optionally substituted C_{1-30}-alkenylcarbonyl, and optionally substituted arylcarbonyl;

R3 is an optionally substituted divalent group forming an N-heterocyclic 5-, 6- or 7-membered ring together with the intervening $-C(R1)_2-N(R2)-C(R1)_2-$ group.

In another aspect, there is provided a fouling-release coating system obtained by the method as defined above.

In another aspect, there is provided a fouling-release coating system comprising:

a. a substrate,

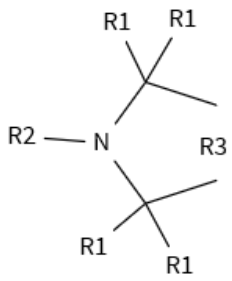
b. optionally one or more primer layers,

c. at least one silicone-containing tie-coat layer

d. a fouling-release layer comprising a condensation-cured polysiloxane-based binder matrix constituting at least 40 % by dry weight of said coat, wherein more than 65 % by weight of said binder matrix is represented by polysiloxane parts, said coat comprising constituents having poly(oxyalkylene) chains,

wherein said tie-coat layer and/or said fouling-release layer further comprises one or more sterically hindered amines, in particular 2,2,6,6-tetraalkyl piperidine derivatives,

wherein the sterically hindered amines are hindered amine moieties of the general formula I:



wherein

each R1 is independently linear or branched C_1-C_4 alkyl;

R2 is selected from -H, optionally substituted linear or branched C_{1-30}-alkyl, optionally substituted linear or branched C_{2-30}-alkenyl, optionally substituted aryl, -OH, optionally substituted linear or branched C_{1-30}-alkoxy, optionally substituted linear or branched C_{1-30}-alkenyloxy, optionally substituted aryloxy, optionally substituted linear or branched C_{1-30}-alkylcarbonyl, optionally substituted C_{1-30}-alkenylcarbonyl, and optionally substituted arylcarbonyl;

R3 is an optionally substituted divalent group forming an N-heterocyclic 5-, 6- or 7-membered ring together with the intervening $-C(R1)_2-N(R2)-C(R1)_2-$ group.

Further details of the disclosure are set out in the dependent claims and the following description.

DETAILED DISCLOSURE

In a first aspect, a method is provided for establishing a fouling-release coating system on a surface of a substrate.

The term "substrate" is intended to mean a solid material onto which a coating composition may be applied. The substrate typically comprises a metal such as steel, iron, aluminium, or a glass-fibre. In the most interesting embodiments, the substrate is a metal substrate, in particular a steel substrate. In an alternative embodiment, the substrate is a glass-fibre substrate.

The term "surface" is used in its normal sense, and refers to the exterior boundary of an object upon which the fouling-release coating system of the invention is applied. As such, the surface of the substrate may either be the "native" surface (e.g. the steel surface). However, the substrate is typically coated, e.g. with an anticorrosive coating, so that the surface of the substrate is constituted by such a coating. Alternatively, the substrate may carry a paint coat, e.g. a worn-out antifouling coat or similar. When present, the anticorrosive coat is typically applied in a total dry film thickness of 100-600 µm, such as 150-450 µm, e.g. 200-400 µm.

Particular examples of surfaces suitable for coating according to the invention are surfaces of vessels (including but not limited to boats, yachts, motorboats, motor launches, ocean liners,

tugboats, tankers, container ships and other cargo ships, submarines, and naval vessels of all types), pipes, shore and off-shore machinery, constructions and objects of all types such as piers, pilings, bridge substructures, water-power installations and structures, underwater oil well structures, nets and other aquatic culture installations, and buoys, etc.

5 *Primer coating*

In a first optional step, the method comprises the applying one or more layers of a primer composition onto the surface of said substrate and allowing said layer(s) to cure, thereby

CLAIMS

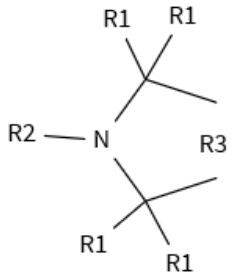
1. A method for establishing a fouling-release coating system on a surface of a substrate comprising the sequential steps of;

a. optionally applying one or more layers of a primer composition onto the surface of said substrate and allowing said layer(s) to cure, thereby forming a primed substrate;

b. applying one or more layers of silicone-containing tie-coat composition in liquid form, onto the surface of said primed substrate or said substrate, and allowing said layer(s) to cure, thereby forming a cured tie-coat layer;

c. applying one or more layers of a fouling-release coating composition onto said cured tie–coat layer, wherein said fouling-release coating composition comprises a condensation-curable polysiloxane-based binder matrix constituting at least 40 % by dry weight of said coating composition, wherein more than 65 % by weight of said binder matrix is represented by polysiloxane parts, and allowing said fouling-release coating composition to cure; wherein said tie-coat composition and/or said fouling-release coating composition comprises constituents having poly(oxyalkylene) chains, and wherein said tie-coat composition and/or said fouling-release coating composition further comprises one or more sterically hindered amines, ~~in particular 2,2,6,6-tetraalkyl piperidine derivatives.~~

~~2. The method according to claim 1,~~ wherein the sterically hindered amines are hindered amine moieties of the general formula I:



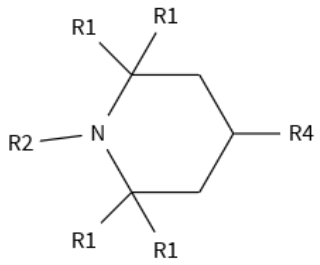
wherein

each R1 is independently linear or branched C_1-C_4 alkyl;

R2 is selected from -H, optionally substituted linear or branched C_{1-30}-alkyl, optionally substituted linear or branched C_{2-30}-alkenyl, optionally substituted aryl, -OH, optionally substituted linear or branched C_{1-30}-alkoxy, optionally substituted linear or branched C_{1-30}-alkenyloxy, optionally substituted aryloxy, optionally substituted linear or branched C_{1-30}-alkylcarbonyl, optionally substituted C_{1-30}-alkenylcarbonyl, and optionally substituted arylcarbonyl;

R3 is an optionally substituted divalent group forming an N-heterocyclic 5-, 6- or 7-membered ring together with the intervening $-C(R1)_2-N(R2)-C(R1)_2-$ group.

~~3~~2. The ~~fouling-release coat~~method according to claim ~~2~~1, wherein the hindered amine moieties are selected from 2,2,6,6-tetraalkyl piperidine moieties of general formula II:



wherein R1 and R2 are defined for general formula I; and R4 represents hydrogen atom(s) or is one or two substituents selected from C_{1-30}-alkyl, C_{1-30}-alkenyl, aryl, C_{1-30}-alkoxy, C_{1-30}-alkenyloxy, aryloxy, C_{1-30}-alkylcarbonyl, C_{1-30}-alkenylcarbonyl, arylcarbonyl, C_{1-30}-alkylcarbonyloxy, C_{1-30}-alkenylcarbonyloxy, and arylcarbonyloxy, in particular from C_{1-8}-alkoxy, C_{1-8}-alkenyloxy, aryloxy, C_{1-8}-alkylcarbonyloxy, C_{1-8}-alkenylcarbonyloxy, and arylcarbonyloxy and/or the attachment point(s) for a polymer, wherein two of said substituents for R4 may form a spiro structure, and wherein the substituent R4 may be linked to one or more hindered amine moieties each independently having the general formula II.

~~4~~3. The method according to claim ~~3~~2, wherein R2 is not H and/or R2 is not -OH.

~~54~~54. The method according to any one of claims ~~32~~32-~~34~~34, wherein the sterically hindered amine(s) comprises 2,2,6,6-tetraalkyl piperidine moieties of the general formula II, and wherein the piperidine derivative(s) are selected from the following types: N-C_{1-30}-alkyl piperidine derivatives, N-C_{1-30}-alkenyl piperidine derivatives, N-aryl piperidine derivatives, N-C_{1-30}-alkoxy piperidine derivatives, N-C_{1-30}-alkenyloxy piperidine derivatives, N-aryloxy piperidine derivatives, N-C_{1-30}-alkylcarbonyl piperidine derivatives, N-C_{1-30}-alkenylcarbonyl piperidine derivatives, and N-arylcarbonyl piperidine derivatives.

~~65~~65. The method according to any one of the preceding claims, wherein hindered amine moieties, in particular 2,2,6,6-tetraalkyl piperidine moieties, are present in the coat in an amount of 0.003-0.5 mol/kg per coating layer.

~~76~~76. The method according to any one of the preceding claims, wherein the sterically hindered amine(s), in particular 2,2,6,6-tetraalkyl piperidine derivative(s), are in liquid form at 20 °C.

~~87~~87. The method according to any one of the preceding claims, wherein the constituent having poly(oxyalkylene) chains is selected from poly(oxyalkylene)-modified alcohols of the general formula (I):

$$(POA–O–)_X–R–(–O–FA)_Y \quad (I)$$

wherein
each POA represents a poly(oxyalkylene) moiety,
each FA represents a C_{8-30} fatty acyl moiety,
R represents the organic residue of an alcohol $R(OH)_{X+Y}$, said organic residue having 2-50 carbon atoms, and
X is 1-5, Y is 0-10 and X+Y is 1-12.

~~98~~98. The method according to any one of the preceding claims, wherein said tie-coat composition comprises one or more cross-linkable polysiloxanes, preferably selected from hydroxy-functional polysiloxanes, C_1-C_4 alkoxy-functional polysiloxanes, amino-functional polysiloxanes and epoxy-functional polysiloxanes.

~~109~~109. The method according to any one of the preceding claims, wherein said tie-coat composition comprises 3-90%, preferably 10-80%, more preferably 20-60%, even more preferably 3-15%, or more preferably more than 40% of said one or more cross-linkable polysiloxanes, by wet weight of the total tie-coat composition.

~~11~~10. The method according to any one of the preceding claims, wherein said tie-coat composition additionally comprises one or more hydrolysable silanes having two or more hydrolysable groups.

~~12~~11. The method according to claim 10, wherein said tie-coat composition comprises up to 30% of said one or more hydrolysable silanes having two or more hydrolysable groups, by wet weight of the total tie-coat composition.

~~13~~12. The method according to any one of the preceding claims, wherein said tie-coat composition comprises one or more epoxy-functional polymers.

~~14~~13. The method according to any one of the preceding claims, wherein said primer composition is an epoxy-based primer composition.

~~15~~14. The method according to any one of the preceding claims, wherein the sterically hindered amine(s), in particular 2,2,6,6-tetraalkyl piperidine derivative(s), are present in a total amount of 0.05-10 % by dry weight of said topcoat composition.

~~16~~15. The method according to any one of the preceding claims, wherein the sterically hindered amine(s), in particular 2,2,6,6-tetraalkyl piperidine derivative(s), are immobilized, e.g. by covalent attachment, to the condensation-curable polysiloxane-based binder matrix or to a filler, e.g. silica.

~~17~~16. The method according to any one of the preceding claims, wherein the poly(oxyalkylene) chains have a number average molecular weight (M_n) in the range of 200-50,000 g/mol.

~~18~~17. The method according to any one of the preceding claims, wherein the constituent having poly(oxyalkylene) chains is selected from poly(oxyalkylene)-modified polysiloxane oils.

~~19~~18. The method according to any one of the preceding claims, wherein the poly(oxyalkylene) chains are covalently attached to the polysiloxane-based binder matrix.

~~20~~19. The method according to any one of the preceding claims, wherein said tie-coat comprises one or more poly(oxyalkylene)-modified polysiloxane oils.

~~21~~20. The method according to any one of the preceding claims, wherein said tie-coat comprises one or more sterically hindered amines as defined in any one of claims 1-5.

~~22~~21. A fouling-release coating system obtained by the method of any of the preceding claims.

~~23~~22. A fouling-release coating system comprising:

a. a substrate,

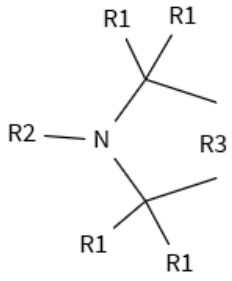
b. optionally one or more primer layers,

c. at least one silicone-containing tie-coat layer

d. a fouling-release layer comprising a condensation-cured polysiloxane-based binder matrix constituting at least 40 % by dry weight of said coat, wherein more than 65 % by weight of said binder matrix is represented by polysiloxane parts, said coat comprising constituents having poly(oxyalkylene) chains,

wherein said tie-coat layer and/or said fouling-release layer further comprises one or more sterically hindered amines, in particular 2,2,6,6-tetraalkyl piperidine derivatives,

wherein the sterically hindered amines are hindered amine moieties of the general formula I:



wherein

each R1 is independently linear or branched C_1-C_4 alkyl;

R2 is selected from -H, optionally substituted linear or branched C_{1-30}-alkyl, optionally

substituted linear or branched C_{2-30}-alkenyl, optionally substituted aryl, -OH, optionally substituted linear or branched C_{1-30}-alkoxy, optionally substituted linear or branched C_{1-30}-alkenyloxy, optionally substituted aryloxy, optionally substituted linear or branched C_{1-30}-alkylcarbonyl, optionally substituted C_{1-30}-alkenylcarbonyl, and optionally substituted arylcarbonyl;

R3 is an optionally substituted divalent group forming an N-heterocyclic 5-, 6- or 7-membered ring together with the intervening $-C(R1)_2-N(R2)-C(R1)_2-$ group.

~~24~~23. The coating system according to claim 22~~23~~, wherein said tie-coat layer comprises one or more poly(oxyalkylene)-modified polysiloxane oils

~~25~~24. The coating system according to any one of claims ~~23~~22-~~24~~23, wherein said tie-coat layer comprises one or more sterically hindered amines as defined in any one of claims 1-5.

~~26~~25. The coating system according to claim ~~25~~24, wherein hindered amine moieties, in particular 2,2,6,6-tetraalkyl piperidine moieties, are present in the tie-coat layer in an amount of 0.003-0.5 mol/kg of the layer.