Abstract:
The invention relates to a composition coating useful for biofouling protection of marine vessels and constructions, for example ships, buoys, platforms, etc. and particularly their underwater parts, preventing the settlement by marine micro-organisms (tubeworms, mussels, barnacles, algae, etc.) and ensure long-term protection against biofouling reducing the deposition of marine micro-organisms (bacterial slime). The coating is suitable for application onto conventional anticorrosion coatings as well as onto metal and non-metal surfaces that do not require anticorrosion protection. The composition coating comprises a combination of room temperature vulcanizing siloxane rubbers with different length of the macromolecular chain; an oil or combination of oils that do not participate in the network formation; a combination of fillers; a solvent; a curing agent and a catalyst of the curing reaction.
COMPOSITION COATING FOR BIOFOULING PROTECTION

FIELD OF INVENTION

The present invention relates to a composition coating for biofouling protection of underwater parts of marine vessels or underwater constructions such as ships, platforms, buoys, pipes, etc. More particularly, this coating prevents the settlement of fouling marine macro-organisms on the surface of static immersed underwater construction as well as of the underwater part of moving vessels, including these moving with low speed (below 14 knots).

BACKGROUND OF THE INVENTION

Composition antifouling paints containing one ore more biocides are well known. Basic disadvantage is their toxicity and the fact that they poison not only the target but also other aquatic organisms.

Non-toxic fouling release coatings called initially "anti fouling" coatings, are also known. US Pat No 4 025 693 discloses antifouling composition coating comprising a mixture of room temperature vulcanizing hydroxyl terminated methyl-phenyl-siloxane rubber with molecular weight of 40 000÷100 000, and cinematic viscosity of 10÷1 000 St, respectively and 1÷10 parts by weight of methyl-phenyl-silicone oil with molecular weight of 2 000÷30 000 and cinematic viscosity of 20÷1 000 cSt, respectively per 100 parts by weight siloxane rubber.

US Pat. No 4 861 670 describes a marine foulers release coating on the base of curing composition containing: 100 parts by weight vinyl end-stopped liquid diorganopolysiloxane with kinematic viscosity of 2 500÷750 000 cSt; 20÷50 parts by weight vinyl functional organopoly(siloxane) co-polymer resin; 1÷200 parts by weight non-reinforcing inorganic filler; platinum catalyst and liquid organohydrosiloxane. Such silicone coating should be applied onto a primed ship hulls to improve the adhesion. Its main disadvantage is that some rest fouling remains after the cleaning of the protected surfaces.

Other patent publications are known which disclose the use of chemically inert oils or greases (slipping agents) in siloxane rubber compositions. German Patent No 1 470 465 describes the use of silicone oils and German Patent No 1 581 727 - of silica free organic compounds, for example polyolefin with molecular weight up to about 5 000, as slipping agents in siloxane rubber fouling release composition coatings. These coatings have the same disadvantage: they only make easy the release of biofoulers without to prevent the settlement.
WO 93/ 13179 describes a composition for protective coating which comprises: (A) a polymer carrying pendant and/or terminal curable functional groups that does not contain siloxane units and (B) a curable organohydropolysiloxane or polydiorganosiloxane, the curable functional groups in component (A) being capable of undergoing a condensation curing reaction with component (B), and normally also a solvent and a curing catalyst.

Another group of patents like for example US Pat. No 5 449 553 and US Pat. No 5 593 732 disclose two-layer protective coating systems with prolonged durability of the protective effect. These protective systems contain underlying tough rubber layer chemically bonded to the fouling releasing top-coat comprising the following components: 90±99 % by weight hydroxyl terminated organopolysiloxane with dynamic viscosity of 1 000÷50 000 cP; 0.1±5 % by weight alkyl silicate and 0.1±5 % by weight curing agent. The releasing top coat contains 10÷300 % by weight filler. The barnacle adhesion to the top coat is low and the detachment of the biofouling is easy by water jet, i.e. such protective coating systems are of the type "biofouling releasing".

EP No 0881269, US Pat. No 6 107 381 and US Pat. No 6 187 447 disclose other room temperature vulcanizing siloxane rubber based protective coatings that only reduce the marine biofouling. According to the first one, the coating composition contains: pre-treated by non-reactive polyorganosiloxane oil reinforcing silica filler in amount of 10÷150 part by weight /100 parts by weight of reactive polyorganosiloxane; at least one condensation curing catalyst (thin-, zirconium- or titancompound) and at least one curing agent to obtain coating composition with dynamic viscosity up to about 10 000 cP. The disclosed in US Pat.No 6 107 381 composition includes free of silanol groups polyorganosiloxan that is able to migrate on the surface and that contains 10÷60 % by weight of at least one hydroxyl or alcoxi terminated polyoxialcylenalcyle radical. According to the thirst patent, the compound that is able to migrate on the surface of the cured polysiloxane contains fluorinated hydrocarbon radical. The described three compositions are suitable for coating of ship hulls to reduce the barnacle adhesion.

US Pat. Appl No 2002 0192181 describes anti-fouling siloxane compositions comprising cured, free of perfluoro-polyether particles, silicone elastomer and liquid fluorinated alkyl- or alcoxy-containing polymer or oligomer.
Other US Pat. Appl. No 2003 0161962 discloses fouling release siloxane composition including curable fluorinated resin. To achieve self cleaning of the based on both these composition coatings, marine vessel speed higher than 14 knots is necessary. Several Japan patents, JP No 06-045170; JP No 61-043668; JP No 06322294 also disclose the use of fluorinated polymers in fouling release coating with similar fouling release effect.

US Pat. No 6 723 376 discloses biofouling inhibition that includes: 1) coating the substrate before exposure in water with a composition that comprises from film-forming polymer (A) with non-reacted silica-containing functional groups ensuring latent reactivity; 2) applying onto this coating of a top layer that contains vulcanizing polymeric material (B) able to inhibit biofouling, namely vulcanizing polysiloxane or fluorocontaining polymer and 3) bonding of the top layer to the underlying coating film by means of condensation curing reaction in which participate non reacted functional groups of the top layer. This double layer inhibiting system has improved mechanical parameters but also does not prevent the settlement of macrofoulers.

All known non-toxic siloxane protective coatings control the marine biofouling by creating of low adhesive surfaces that make difficult its adherence, ensure a self cleaning at moving speed higher than 14 knots and an easy detachment of the biofoulers with a water jet, a brush, or trough a wiping during dry docking. Common disadvantage of these fouling release coatings is that they do not prevent the macro- and micro-fouling and do not self clean at static underwater constructions as well as at slowly moving vessels (a speed lower than 14 knots) and/or at a long docking in the harbors.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the technical level an aspect of this invention is to create a composition coating for biofouling protection that to prevent a settlement of marine macro-organisms and to reduce the microfouling on underwater static working or moving, including slowly moving (speed of less than 14 knots) surfaces.

Solution of the task is a composition biofouling protecting coating based on a combination of room temperature vulcanizing siloxane elastomers.

The protecting coating distinguishes that it comprises: a combination of at least two room temperature vulcanizing α,ω-dihydroxiterminated siloxane elastomers with different
molecular mass in the range of 20 000÷100 000, as the first one is with molecular weight of
20 000-40 000, and the second one - of 60 000÷100 000 and the quantitative ratio between
them is 3:1÷1:2, in amount of 50÷70 % by weight; inert non-participating in the formation of
vulcanization network oil in amount of 10÷40 % by weight; combination of at lest two fillers,
reinforcing and non-reinforcing, in ratio of 1:3÷1:6 in amount of 10÷30 % by weight; a
hydrocarbon solvent for regulation of the viscosity, in amount up to 20 % by weight; at least
one three- or four-functional curing agent in amount of 1÷10 % by weight and at least one
catalyst of condensation curing reaction running at presence of moisture, in amount of 0,1÷1,0
% by weight.

According to one preferable performance of the invention, the biofouling protective
coating is composed on the base of room temperature vulcanizing siloxane elastomers and
characterizes that contains: a combination of three room temperature vulcanizing α,ω-
dihydroxiterminated siloxane elastomers with different molecular mass in the range of
20 000÷100 000, as the first one is with molecular weight of 20 000÷30 000, and the second
one - of 40 000÷50 000 and the third one - of 70 000÷100 000 in a quantitative ratio between
them is 3:20:1, in amount of 50÷70 % by weight; inert non-participating in the formation of
vulcanization network oil in amount of 20÷30 % by weight; combination of at lest two fillers,
reinforcing and non-reinforcing, in ratio of 1:4 in amount of 15÷20 % by weight; a
hydrocarbon solvent for regulation of the viscosity, in amount up to 50 % by weight; at least
one three- or four-functional curing agent in amount of 1÷10 % by weight and at least one
catalyst of condensation curing reaction running at presence of moisture, in amount of 0,1÷1,0
% by weight.

One variant performance of the composition coating for prevention of macrofouling
characterizes with this that the non reactive oil is three-methylterminated siloxane oil with
molecular mass of 10 000÷20 000 (dynamic viscosity of 200÷500 cP) or perfluoropolyether
fluorinated oil with at least 10÷30 perfluoropolyether units (cinematic viscosity of 10÷500
cSt) or a combination of both in weight ratio 10:1÷1:10.

It is preferable as a reinforcing filler to be used silica type filler and the non-
reinforcing filler to be carbonate type.
It is suitable the reinforcing silica filler to be fine dispersed or flecks or a combination of both, in weight ratio of 1:10÷10:1 and the disperse carbonate filler to be micron- or nano-carbonate.

It is suitable also the fillers to be pre-treated in oxygen or ozone-containing cold plasma of barrier discharge in vacuum (1-200 Pa) or at atmospheric pressure at room temperature and at frequency of 50 Hz-200 kHz for 15-90 sec.

Tetra-ethoxisilane, methyl-three-etoxisilane or ES40 (ethoxi-oligosiloxane) are preferable as a three- or tetra-functional curing agent.

As a catalyst of the condensation curing reaction can be used organic metallic tetra-functional compound with a general formula: $R_{n-m}M^n(OCOR')_m$, where: $M = Sn, Pb, Ni, Co, Fe, Cd, Cr, Mn, Zn, Al, Zr$; $n = 2-4$; $m = 2-4$; $R' = alkyl$ with $C,-Ci_7$ or $Ti(C_4Ho)_4$, for example di-butylthin di-laurate, tetra-butyltitanat, etc.

Main advantage of the composition coating for biofouling protection according to the invention is that it does not allow marine macroorganisms settlement and in significant degree reduces the accumulation of microorganisms onto surfaces working under water in static conditions or at low and high speeds of movement.

The application of the composition coating for biofouling protection according to the invention is easy by brushing; rolling or spraying onto the conventional anticorrosion coatings, metal- or other surfaces, do not requiring anticorrosion protection; also as a top-coat onto tough underlying substrate ensuring mechanical strength and durability of the biofouling protective system.

EXAMPLES

Further on, the invention will be illustrated by example performances of the protective coating that do not limit the creation and use of other composite components of the coating having equivalent parameters and properties ensuring the enrichment of the given useful properties of the protective coating objective of this invention.

The invention is illustrated by the following examples. All ratios and percentage are by weight.
EXAMPLE 1

Steel plate having anticorrosion coating on a base of unsaturated polyester resin (EX-PEK 1704.05, Firm "Emajlchim" AD, Bulgaria) is treated with primer (silane, A 1100, Dow Corning Ltd.), and after that is coated by rolling with 200 μm thick layer of composition consisting of: a combination of two RTV α,ω-dihydroxipolydimetyle siloxanes with molecular weights of 50 000 and 90 000, respectively in ratio 22:1 - 60 %; threemethylsilox terminated silicone oil with dynamic viscosity of 350 cP (PMS 350, Firm ZPG "Kremnijpolymer", Ykraina) —25 %; combination of two fillers, silica filler (Aerosil 200, Degusa) and calcium carbonate precipitate, (Hôchst GmBh) in ratio 1:4 —14 %; titan dioxide - 0,5 % for white coloring. Room temperature vulcanization performs with 4 % of a curing agents system containing ES 40, (ZPG"Kremnijpolymer", Ykraina) and di-bytilthin di-laurate (Aldrich Chem. Corp.) as a catalyst, in ratio of 10:1.

After a room temperature curing, the sample immerses in marine water and the settlement monitors monthly. The antifouling rating is 100 after 3 and 6 month keeping in the water, i.e. a macro-fouling is totally missing.

This result is confirmed also by an exposure of cured coating composition sample coupons (thickness of 3 mm) for 18 month under the conditions of the very intensive biofouling in Indian Ocean, Fishing harbor, Chennai. No macro-fouling is observed after this immersion in static conditions.

EXAMPLE 2

Steel plate having anticorrosion coating on a base of unsaturated polyester resin (EX-PEK 1704.05, Firm "Emajlchim" AD, Bulgaria) is treated with primer (silane, A 1100, Dow Corning Ltd.), and after that is coated by rolling or brushing with 250 μm thick layer of composition consisting of: a combination of three RTV α,ω-dihydroxipolydimetyle siloxanes with molecular weights of 50 000, 35 000 and 90 000, respectively in ratio 20:3:1 - 60 %; three-methylsilox terminated silicone oil with dynamic viscosity of 350 cP (PMS 350, Firm ZPG "Kremnijpolymer", Ykraina) - 25 %; combination of two fillers, silica filler (Aerosil 200, Degusa) and calcium carbonate precipitate, (Hôchst GmBh) in ratio 1:4 - 14 %; titan dioxide - 0,5 % for white coloring. Room temperature vulcanization performs with 4 % of a curing agents system containing ES 40, (ZPG"Kremnijpolymer", Ykraina) and di-bytilthin di-laurate (Aldrich Chem. Corp.) as a catalyst, in ratio of 10:1.
After a room temperature curing, the sample immerses in marine water and the settlement monitors monthly. The antifouling rating is 100 after 3 and 6 month keeping in the water, i.e. a macro-fouling is totally missing.

This result is confirmed also by an exposure of cured coating composition sample coupons (thickness of 3 mm) for 18 month in the conditions of the very intensive biofouling in Indian Ocean, Fishing harbor, Chennai. No macro-fouling is observed after this immersion in static conditions.

EXAMPLE 3

Alumina plate having vinyl anticorrosion coating (EX-VEL 1504.02, Firm "Emajlchim" AD, Bulgaria) is treated with primer (C 03, Firm ZPG "Kremnijpolymer", Ykraina), and after that is coated by rolling or brushing with 200 µm thick layer of composition consisting of: a combination of three RTV α,ω-dihydroxypolydimetyle siloxanes with molecular weights of 50 000, 35 000 and 90 000, respectively in ratio 20:3:1 - 60 %; threemethylsiloxo terminated silicone oil with dynamic viscosity of 350 cP ( PMS 350, Firm ZPG "Kremnijpolymer", Ykraina) - 15 % and fluorinated oil (Krytox GPL 105, DuPont Ltd) —10 %; combination of two fillers, silica filler (Aerosil 200, Degusa) and calcium carbonate precipitate, (Hochst Gmbh) in ratio 1:4 - 14 %; titan dioxide - 0,5 % for white coloring. Room temperature vulcanization performs with 4 % of a curing agents system, containing ES 40, (ZPG"Kremnijpolymer", Ykraina) and di-bytilthin di-laurate (Aldrich Chem. Corp.) as a catalyst, in ratio of 10:1.

After a room temperature curing, the sample immerses in ocean water and the settlement monitors monthly. The antifouling rating is 100 after 3 and 6 month keeping in the water, i.e. a macro-fouling is totally missing.

This result is confirmed also by an exposure of cured coating composition sample coupons (thickness of 3 mm) for 18 month in the conditions of the very intensive biofouling in Indian Ocean, Fishing harbor, Chennai. No macro-fouling is observed after this immersion in static conditions.

EXAMPLE 4

Wood plate having polyester lack coating (EX-PEK 1704.03, Firm "Emajlchim" AD, Bulgaria) is treated with primer (silane, A 1100, Dow Corning Ltd.), and after that is coated by rolling or brushing with 300 µm thick layer of composition consisting of: a combination of
ttree RTV α,ω-dihydroxipolydimethylsiloxanes with molecular weights of 50,000, 35,000 and 90,000, respectively in ratio 20:3:1 - 60%; three-methylsiloxy terminated silicone oil with dynamic viscosity of 350 cP (PMS 350, Firm ZPG "Kremnijopolymer", Ukraina) - 24%; combination of two fillers, silica filler (Aerosil 200, Degusa) and nano calcium carbonate, pre-activated by cold plasma treatment at atmospheric pressure at 10 kHz and 15 kV for 60 sec, in ratio 1:4 - 14%; titan dioxide - 0.5% and phthalocyanine blue - 2% for blue coloring. Room temperature vulcanization performs with 4% of a curing agents system containing ES 40, (ZPG"Kremnijopolymer", Ukraina) and di-bytilthin di-laurate (Aldìch Chem. Corp.) as a catalyst, in ratio of 10:1.

After a room temperature curing, the sample immerses in ocean water and the settlement monitors monthly. The antifouling rating is 100 after 3 and 6 month keeping in the water, i.e. a macro-fouling is totally missing.

This result is confirmed also by an exposure of cured coating composition sample coupons (thickness of 3 mm) for 18 month in the conditions of the very intensive biofouling in Indian Ocean, Fishing harbor, Chennai. No macro-fouling is observed after this immersion in static conditions.
CLAIMS

1. A composition coating for biofouling protection on a base of room temperature vulcanizing siloxane elastomers which characterizes that contains: a combination of at least two room temperature vulcanizing α,ω-di-hydroxipolydimethyl siloxanes with different molecular weights in the range of 20 000÷100 000, the first one having molecular weight of 20 000÷40 000, the second one - of 60 000÷100 000, in ratio by weight of 3:1÷1:2 - 50÷70 % by weight; non-bonding to the vulcanization network oil - 10÷40 % by weight; combination of at least two fillers, reinforcing and non-reinforcing, in ratio by weight 1:3÷1:6 - 10÷30 % by weight; hydrocarbon solvent for the viscosity regulation - up to 20 % by weight; at least one three- or four-functional curing agent in amount of 1÷10 % by weight and at least one catalyst of condensation type moisture curing reaction in amount of 0,1÷1,0 % by weight.

2. A composition coating for biofouling protection, according to claim 1, on the base of room temperature vulcanizing siloxane elastomers characterizing with this that it contains: a combination of at least three room temperature vulcanizing α,ω-di-hydroxipolydimethyl siloxanes with different molecular weights in the range of 20 000÷100 000, the first one having molecular weight of 20 000÷30 000, the second one - of 40 000÷50 000, and the third - of 70 000÷100 000, in ratio by weight of 3:20:1 - 50÷70 % by weight; non-bonding to the vulcanization network oil or combination of oils - 20÷30 % by weight; combination of at least two fillers, reinforcing and non-reinforcing in ratio by weight 1:4 - 15÷20 % by weight; hydrocarbon solvent for the viscosity regulation - up to 50 % by weight; at least one three- or four-functional curing agent in amount of 1÷10 % by weight and at least one catalyst of condensation type moisture curing reaction in amount of 0,1÷1,0 % by weight.

3. A composition coating for biofouling protection, according to claims 1 and 2 wherein the oil is three-methylsiloxytherminated siloxane oil with molecular weight of 10 000÷20 000 (dynamic viscosity of 200÷500, respectively) or perfluoropolyether fluorinated oil having 10-30 perfluoropolyether units (cinematic viscosity of 10÷500 cSt, respectively) or combination of both in ratio by weight 10:1÷1:10.
4. A composition coating for biofouling protection, according to claims 1, 2 and 3 wherein
the reinforcing filler is silica type and the non-reinforcing one is carbonate type,
5. A composition coating for biofouling protection, according to claims 1, 2, 3 and 4 wherein
the reinforcing filler is fine disperse or flacks, or combination of both in ratio by weight
10:1±1:10 and the non-reinforcing filler is micron or nano carbonate.
6. A composition coating for biofouling protection, according to claims 1, 2, 3, 4 and 6
wherein the fillers can be pre-treated in cold plasma of barrier electrical discharge in vacuum
(1±200 Pa) or at atmospheric pressure at frequency of 50Hz±200 kHz and a treatment
duration of 15±90 sec.
7. A composition coating for biofouling protection, according to claims 1, 2, 3, 4, 5 and 6
wherein the cold plasma of the barrier dielectric discharge is ozone- or oxygen-containing
plasma.
8. A composition coating for biofouling protection, according to claims 1, 2, 3, 4, 5, 6 and 7
wherein the terra- and three-functional curing agents are tetra-ethoxisilane, methyl-three-
ethoxisilane or ES40 (ethoxi-oligo-silanes), respectively.
9. A composition coating for biofouling protection, according to claims 1, 2, 3, 4, 5, 6, 7 and
8 wherein the catalyst of the condensation curing reaction is organo-metallic tetra-functional
compound with general formula: \( R_{n-m} M^n(0C0R')_m \), where: \( M = Sn, Pb, Ni, Co, Fe, Cd, Cr, \\
Mn, Zn, Al, Zr; n = 2-4; m = 2÷4; R' = alkyl with \( C_1-C_n \) or \( Ti(OC_4Hg)_4 \), for example di-
butylthine di-laurate, tetra-butyltitanat, etc.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both national classification and IPC:

INV. C09D183/04 C09D5/16

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C.

See patent family annex.

Date of the actual completion of the international search

28 August 2007

Date of mailing of the international search report

04/09/2007

Name and mailing address of the ISA

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