

SPECIFICATION

TITLE OF THE INVENTION

Preventive Agents against Adhesion of Marine Organisms and
Methods of Preventing Such Adhesion of Marine Organisms

5 BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to preventive agents
against adhesion of marine organisms and methods to prevent
such adhesion. Particularly, the preventive agents and
10 methods can effectively protect seawater-drawing pipes,
fishing nets, bottoms of ships and structures in the sea
against fouling caused by marine organisms, especially
serpulidae, by applying the agents to articles or struc-
tures, or adding them into seawater systems.

15 2. Description of Related Art

Recently, an increasing number of marine organisms,
especially serpulidae, have been observed adhering in semi-
closed bays and maricultures. In some factories using
seawater as cooling water, they adhere to the insides of
20 tubes of heat exchangers, causing pitting or corrosion. In
some maricultures, they sometimes do great damage to oyster
farm; and they sometimes adhere in a large number to culture
fish crawl nets, obstruct a flow of seawater, cause dis-

solved oxygen to become in short supply in the crawls, resulting in death of bred fishes. When they adhere to the bottom of a ship, they reduce speed of the ship, giving such trouble that the ship must be docked for removal of them.

5 Conventionally, for protecting such seawater pipes, ships and fishing nets, a chlorine-base agent and an anti-fouling agent containing an organic tin compound or cuprous oxide were generally used. Since such compounds was toxic to marine organisms, serpulidae were prevented together with
10 barnacles and mussels of Mytilus edulis galloprovincialis, Perna viridis and the like. However, because these anti-fouling agents containing metal are slow in degrading in the environment and also accumulates into organisms, use thereof has been restricted for preserving the environment. There-
15 fore, development of an alternative safe antifouling agent is highly anticipated. As safety of compounds has been pursued, it has been obvious that the difference in effects of the agents on individual marine adherent organisms.

20 From the above point of view, higher aliphatic amine compounds have been proposed as safe preventive agents against adhesion of marine organisms (see Japanese Patent Publications Nos. SHO 56(1981)-3842, SHO 59(1984)-20641, SHO 60(1985)-23641, SHO 60(1985)-52726 and Japanese Unexamined Patent Publications Nos. HEI 1(1989)-197407 and HEI

4(1992)-41403).

5 The higher aliphatic amine compound as a safe preventive agent against marine adherent organisms is known to have potent effects of preventing adhesion of mussels of Mytilus edulis galloprovincialis, and barnacles. However, when used to prevent adhesion of serpulidae, it must be poured into a seawater system at a high concentration and, when used as antifouling agent, it must disperse from anti-fouling coating at a high concentration. That may cause environmental contamination and also is not preferable from economical viewpoint.

10 Serpulidae are marine adherent organisms belonging to Serpulidae family of Polychaeta class of Annelida phylum on the classification system. Their larvae swim in the sea and, when they touch suitable attached bases, they adhere to them, where they grow forming calcareous tubes with secretion. Sometimes such tubes grow to be more than 10cm in thickness for about 2 months. Therefore, the serpulidae are considered to be one of the marine adherent organisms which cannot be removed easily.

SUMMARY OF THE INVENTION

The present invention, in view of the above circumstances, is to provide a preventive agent effective against adhesion of serpulidae which is harmless to man, animals,

fishes and shellfishes, and is unlikely to contaminate the environment, and to provide a preventive method using the same. The preventive agent and method can be used on a fishing nets, water pipes and other structures in the sea area where adhesion of serpulidae is particularly observed.

The inventors, by having keen study on preventive agents effective against adhesion of serpulidae which hardly affect the environment, have found that combined use of at least two kinds of amine compounds in a remarkably small amount outperforms by comparison with single use of an individual amine compound in preventing the adhesion, and also have found the combined use prevents adhesion of other marine organisms in a similar amount.

The present invention, based on the above findings, provides a preventive agent against adhesion of a marine organism comprising:

at least one amine compound represented by the following formula (I):



, wherein R is a C₈₋₂₂ saturated or unsaturated aliphatic hydrocarbon group, R¹ is hydrogen atom, aminopropyl, a C₁₋₂₂ saturated aliphatic hydrocarbon or C₂₋₂₂ unsaturated aliphatic hydrocarbon group, R² is aminopropyl, a C₁₋₈

saturated aliphatic hydrocarbon or C₂₋₈ unsaturated aliphatic hydrocarbon group, provided that R¹ is hydrogen atom or aminopropyl group when R² is aminopropyl group, or a salt thereof; and

5 at least one N-alkyl polyamine compound represented by the following formula (II):



10 , wherein R is a C₈₋₂₂ saturated or unsaturated aliphatic hydrocarbon group and n is an integer from 2 to 4, or a salt thereof in an amount of 0.1 to 9 parts by weight to one part by weight of the compound (I).

15 Further, the present invention provides a method of preventing adhesion of a marine organism comprising a simultaneous or separate adding to an objective seawater system subjected to antifouling of at least one amine compound (I) or a salt thereof and at least one N-alkyl polyamine compound (II) or a salt thereof at a concentration of 0.001 to 0.2mg/L of seawater as the active ingredient.

20 The active ingredients of the invention are considered to have the following mechanism of preventing the adhesion: The amine compound of the formula (I) as well as the N-alkyl-polyamine compound of the formula (II), when existing individually, is readily adsorbed by an anion component

such as suspended matter in water. Therefore, it cannot keep its dispersed state so that it does not act on target marine adherent organisms. However, simultaneous existence of these two compounds inhibits the adsorption and keeps the dispersed state, working effectively on marine adherent organisms such as serpulidae. Thus the ability to prevent the adhesion is enhanced.

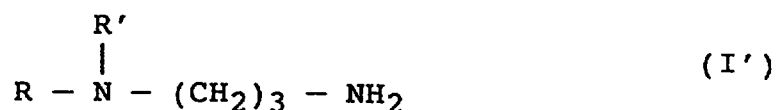
DESCRIPTION OF THE PREFERRED EMBODIMENTS

The marine adherent organisms according to the invention includes serpulidae, barnacles, mussels such as Mytilus edulis galloprovincialis, Perna viridis and the like. Especially the serpulidae.

The objective system in seawater according to the invention includes 1) seawater aqueducts such as cooling seawater tubes in iron manufacturing factories, 2) fishing nets and facilities in maricultures, and 3) structures in the sea such as the bottoms of ships and bridges.

The compounds represented by the formulae (I) and (II) which are active ingredients of the invention are known, for which commercially available products may be used.

Preferred class of the compounds (I) is represented by the sub-formula (I'):



, wherein R is the same as defined in the formula (I) and R' is hydrogen atom or aminopropyl group.

Other preferred class of the compounds (I) is represented by the sub-formula (I''):



, wherein R is the same as defined in the formula (I), R_a is a C_{1-22} saturated aliphatic hydrocarbon or C_{2-22} unsaturated aliphatic hydrocarbon group, and R_b is a C_{1-8} saturated aliphatic hydrocarbon or C_{2-8} unsaturated aliphatic hydrocarbon group. The compound or compounds belonging to either one or both of these two classes may be used.

Examples of the C_{8-22} saturated or unsaturated aliphatic hydrocarbon groups represented by R in the formulae (I) and (II) are alkyl groups such as octyl, decyl, dodecyl, hexadecyl and octadecyl, and alkenyl groups such as oleyl, coconut alkyl, beef tallow alkyl, hardened beef tallow alkyl and soybean alkyl.

Examples of the C_{1-22} saturated aliphatic hydrocarbon groups represented by R^1 in the formula (I) or by R_a in the sub-formula (I') are methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, coconut alkyl, beef tallow alkyl, hardened beef tallow alkyl and soybean alkyl.

Examples of the C_{2-22} unsaturated aliphatic hydrocarbon group represented by R^1 or R_a are vinyl, propenyl, butenyl, pentenyl, hexenyl, myristeyl, palmiteyl, oleyl, linoleyl, coconut alkyl, beef tallow alkyl, hardened beef tallow alkyl and soybean alkyl.

Examples of the C_{1-8} saturated aliphatic hydrocarbon group represented by R^2 of the formula (I) or by R_b of the sub-formula (I") are methyl, ethyl, propyl, butyl, pentyl, hexyl and octyl. Examples of the C_{2-8} unsaturated aliphatic hydrocarbon groups represented by the same symbols are vinyl, propenyl, butenyl, pentenyl, hexenyl and octenyl. The above-mentioned alkyl groups include all the isomers thereof.

The coconut alkyl, beef tallow alkyl, hardened beef tallow alkyl and soybean alkyl groups here are C_{12-20} saturated or unsaturated straight or branched chain aliphatic hydrocarbon groups produced with a known process from coconut oil or coconut fat, beef tallow and soybean oil respectively.

Specific examples of the compounds of the formula, especially those of the sub-formula (I') are N-dodecyl-propylenediamine, N-hexadecyl-propylenediamine, N-octadecyl-propylenediamine, N-oleyl-propylenediamine, N-coconut alkyl-propylenediamine, N-beef tallow alkyl-

propylenediamine, N-hardened beef tallow alkyl-propylenedi-
 amine, N-dodecyl-N,N-bis(3-aminopropyl)amine, N-hexadecyl-
 N,N-bis(3-aminopropyl)amine, N-octadecyl-N,N-bis(3-aminopro-
 pyl)amine, N-oleyl-N,N-bis(3-aminopropyl)amine, N-coconut
 5 alkyl-N,N-bis(3-aminopropyl)amine, N-beef tallow alkyl-N,N-
 bis(3-aminopropyl)amine and N-hardened beef tallow alkyl-
 N,N-bis(3-aminopropyl)amine, or salts thereof.

Specific examples of the compounds of the sub-formula
 (I") for the formula (I) are dodecyldimethylamine, tetra-
 10 decyldimethylamine, hexadecyldimethylamine, octadecyldi-
 methylamine, oleyldimethylamine, soybean alkyl dimethyl-
 amine, beef tallow alkyl dimethylamine, coconut alkyl di-
 methylamine, didodecylmethylamine, ditetradecylmethylamine,
 dihexadecylmethylamine, dioctadecylmethylamine, di(beef
 15 tallow alkyl)methylamine, di(coconut alkyl)methylamine,
 dodecyltetradecylmethylamine, dodecylhexadecylmethylamine,
 dodecyloctadecylmethylamine, tetradecylhexadecylmethylamine,
 tetradecyloctadecylmethylamine, hexadecyloctadecylmethyl-
 amine, dodecylmethylpropylamine, hexadecylmethylethylamine,
 20 beef tallow alkyl ethylpropylamine, beef tallow alkyl
 diethylamine, beef tallow alkyl dipropylamine, beef tallow
 alkyl methylhexylamine, coconut alkyl dipentylamine and
 coconut alkyl dihexylamine, or salts thereof.

Specific examples of the compounds of the formula (II)
 25 are N-dedecyl-dipropylenetriamine, N-hexadecyl-dipropylene-

triamine, N-octadecyl-dipropylenetriamine, N-oleyl-dipropylenetriamine, N-coconut alkyl dipropylenetriamine, N-beef tallow alkyl-dipropylenetriamine, N-hardened beef tallow alkyl-dipropylenetriamine, N-dodecyl-tripropylene-
5 tetraamine, N-hexadecyl-tripropylene-tetraamine, N-octadecyl-tripropylene-tetraamine, N-oleyl-tripropylene-tetraamine, N-coconut alkyl-tripropylene-tetraamine, N-beef tallow alkyl-tripropylene-tetraamine, N-hardened beef alkyl-tripropylene-tetraamine, N-tetradecyl-tetrapropylene-penta-
10 amine, N-coconut alkyl-tetrapropylene-pentaamine, N-hexadecyl-tetrapropylene-pentaamine, N-octadecyl-tetrapropylene-pentaamine and N-beef tallow alkyl-tetrapropylene-pentaamine, or salts thereof.

Usable acids for forming these salts are inorganic
15 acids such as hydrochloric, hydrobromic, nitric, sulfuric or phosphoric acid; organic acids such as formic, acetic, oleic, naphthenic, adipic, lactic, citric or benzoic acid, and anionic residues of saccharin.

The preventive agent against adhesion of marine organ-
20 isms of the present invention comprises a combination of the compound of the formula (I) and the compound of the formula (II). Preferable examples of the combination are as follows:

(1) The combination of the compound of the formula (I),

especially the sub-formula (I'), and the compound of the
 formula (II) are N-coconut alkyl propylenediamine and N-beef
 tallow alkyl-tripropylenetetraamine, N-beef tallow alkyl
 propylenediamine and N-oleyl-tripropylenetetraamine, N-
 5 hexadecyl-propylenediamine and N-octadecyl-dipropylenetri-
 amine, N-beef tallow alkyl-N,N-bis(3-aminopropyl)amine and
 N-dodecyl-tripropylenetetraamine, N-octadecylpropylenedi-
 amine and N-coconut alkyl-dipropylenetriamine, N-hexadecyl-
 propylenediamine and N-beef tallow alkyl-dipropylenetri-
 10 amine, N-beef tallow alkyl-propylenediamine and N-
 dodecyl-tripropylenetetraamine, N-coconut alkyl propylene-
 diamine and N-hexadecyl-tripropylenetetraamine, N-beef
 alkyl-N,N-bis(3-aminopropyl)amine and N-coconut alkyl-
 dipropylenetriamine, N-oleyl-propylenediamine and N-beef
 15 tallow alkyl-dipropylenetriamine, N-oleyl-propylenediamine
 and N-beef tallow alkyl-tetrapropylenepentaamine, N-oleyl-
 N,N-bis(3-aminopropyl)amine and N-beef tallow alkyl-tetra-
 propylenepentaamine, and N-coconut alkyl-propylenediamine
 and N-beef tallow alkyl-tetrapropylene-pentaamine.

(2) The combinations of the compound of the formula
 (I), especially the sub-formula (I"), and the compound of
 the formula (II) are dodecyldimethylamine and N-coconut
 alkyl-dipropylenetriamine, beef tallow alkyl dimethylamine
 and N-dodecyl-tripropylenetetraamine, oleyldimethylamine and
 25 N-beef tallow alkyl-dipropylenetriamine, hexadecyldimethyl-

amine and N-oleyl-tripropylenetetraamine, and soybean alkyl dimethylamine and N-octadecyl-tetrapropylenepentaamine.

(3) The combinations of the compound of the formula (I), especially the compounds of the sub-formula (I') and the sub-formula (I''), with the compound of the formula (II) are N-oleyl-propylenediamine and didodecylmethylanine with N-coconut alkyl-dipropylenetriamine, N-beef tallow alkyl-N,N-bis(3-aminopropyl)amine and soybean alkyl dimethylamine with N-octadecyl-tripropylenetetraamine, N-dodecyl-propylenediamine and oleyldimethylamine with N-tetradecyl-tetrapropylenepentaamine, N-hexadecyl-propylenediamine and beef tallow alkyl-dimethylamine with N-hexadecyl-dipropylenetriamine, N-coconut alkyl- N,N-bis(3-aminopropyl)amine and oleyldimethylamine with N-octadecyl-tripropylenetetraamine, N-soybean alkyl-N,N- bis(3-aminopropyl)amine and oleyldimethylamine with N-beef tallow alkyl-tripropylene-tetraamine, and N-dodecyl-propylenediamine and tetradecyl-hexadecylmethylanine with N-tetradecyl-tetrapropylenepentaamine.

Alternatively, the respective salts of the above amines or at least one of them may be used in the combination.

The preventive agent against adhesion of marine organisms according to the invention contains the compound of the formula (II) at a ratio from 0.1 to 9 parts by weight,

preferable from 0.2 to 8 parts by weight, with respect to 1 part by weight of the compound of the formula (I).

When the compounds of the sub-formulae (I') and (I'') are used together as the compound of the formula (I), they are preferably contained at a weight ratio from 1:10 to 10:1 for antifouling and antifoaming.

The compound of the sub-formula (I''), particularly, has the ability to inhibit foaming which results from the compounds of the formula (I') and (II), or from the compound of the formula (II), and therefore is suitable to use on a preventive object system wherein foaming may cause trouble.

Preferably, the preventive agent against adhesion of marine organisms of the invention is usually prepared in a liquid formulation, but not limited thereto depending on an object for which it is used.

When the objective system is a cooling seawater system, the preventive agent is preferably in the form of an aqueous formulation. Such a formulation can be prepared using a conventional method by mixing the active ingredients of the invention with water or a hydrophilic organic solvent and, if necessary, adding a surfactant.

Examples of the hydrophilic organic solvents are ethanol, propanol, isopropanol, butyl diglycol, ethylene glycol and propylene glycol monomethyl ether. These hydrophilic organic solvents may be used as a mixture with water.

Examples of the surfactants are polyoxyethylene alkyl ethers, polyoxyethylene alkyl esters, polyoxyethylene sorbitan alkyl esters, polyoxyethylene polyoxypropylene copolymer and alkylbetaines.

5 When used for a fishing net or the like, the preventive agent is preferably prepared in a liquid-type formulation. That is, the active ingredients of the invention are prepared by a conventional method into the antifouling agent by using an organic solvent as a medium and optionally adding a
10 film-forming agent, plasticizer, coloring agent and the like.

 Examples of the above organic solvents are ethanol, butanol, xylene, toluene, kerosene, methylisobutylketone, butyl acetate, naphtha and propylene glycol monomethyl
15 ether. Other various solvents which are used for paints may be used. -A little amount of water can also be contained.

 Examples of the film-forming agents such as natural or synthetic resins are rosin resin, coumarone resin, polybutene, polyvinyl chloride, polybutyral and acrylic resin.

20 Examples of the plasticizers are liquid paraffin, nonylphenol, dioctyl phthalate, diadipate phthalate and trioctyl phosphate.

 It is preferred that the antifouling agent used for fishing net contains 10 to 30 wt% active ingredients, 3 to

30 wt% film-forming agent, 0 to 10 wt% plasticizer and an organic solvent at the remaining percentage with the whole solid concentration being 25 to 60 wt%, considering the film-formation and strength of the film.

5 The antifouling agent is used for fishing net by dipping or coating.

 Further, when used for the bottom of a ship or a structure in the sea, the preventive agent may be prepared into a antifouling coating by further adding pigments to the above
10 antifouling agent for fishing net.

 Examples of the pigments are talc, titanium white, chrome yellow, Prussian blue, red oxide and phthalocyanine blue.

 The antifouling coating may contain 10 to 30 wt% of the
15 active ingredients, 3 to 25 wt% of the film-forming agent, 0 to 10 wt% of the plasticizer and 10 to 30 wt% of the pigment.

 The antifouling coating is aptly applied to various marine structures by brushing, spraying and the like. The
20 preventive agent of the invention thus applied exhibits long-term effects with antifouling film being formed with drying.

 The antifouling active ingredients of the invention may be optionally used as a mixture with a known antifouling
25 agent such as copper naphthenate, copper oleate, dimethyl-

dithiocarbamate, tetraethyluram disulfide, zinc pyrithione, 2,3-dichloro-N-(2',6'-diethylphenyl)maleimide and 4,5-dichloro-2-n-octylisothiazolin-3-one.

5 The method of preventing adhesion of marine organisms according to the invention is as mentioned above.

In the method of the invention, the above-described active ingredients, when simultaneously added, are more easily used in a single formation, but the effects are the same when they are separately added. Also in this case,
10 they are preferably prepared into a formation suitable for use as described above.

In the method of the invention, the addition amount of the active ingredients may vary depending on the objective seawater systems, but is usually sufficient at a concentra-
15 tion of about 0.001 to about 0.2mg/L of seawater, preferably about 0.003 to about 0.1mg/L.

The active ingredients, when used for a cooling seawater system in particular, are poured for 12 to 24 hours per day in the above addition amount with respect to a flow
20 rate of seawater, with good effects. The addition amount may slightly vary according to states of the sea water, and is preferably increased when a lot of serpulidae grow. However, the concentration up to 0.5mg/L of seawater may be sufficient in any condition, and the concentration exceeding

the limit is not preferred from an environmental and economical point of view.

In the method of the invention, other known antifouling agents may be used together as previously described.

The present invention will be hereinafter described in detail with reference to the following formulation examples, test examples and comparative examples, but these examples are not to be construed to limit the scope of the invention.

5 Formulation Examples

The formulations of the invention were made into emulsion or water-soluble type. For the emulsion type, the amine compounds were dissolved in isopropyl alcohol, to which Toxanon P-900 (Trademark, manufactured by Sanyo Chem. Ind., Ltd., Japan, nonionic and anionic surfactant HLB>12) was added for emulsifying. For the water-soluble type, the amine compounds were equimolecularly reacted with hydrochloric acid, acetic acid or other organic acid to form aqueous formulation.

15 Formulation 1 (Table 1, Example 1)

N-Coconut alkyl-propylenediamine	15%
N-Beef tallow alkyl-tripropylenetetraamine	15%
Hydrochloric acid	9%
Isopropyl alcohol	10%
20 Water	51%

Formulation 2 (Table 1, Example 2)

N-Beef tallow alkyl-propylenediamine	25%
N-Oleyl-tripropylenetetraamine	5%
Acetic acid	2.5%

Toxanon P-900 (HLB>12)	25%
Diethyleneglycol monomethyl ether	42.5%

Formulation 3 (Table 1, Example 3)

	N-Hexadecyl-propylenediamine	20%
5	N-Octadecyl-dipropylenetriamine	10%
	Toxanon P-900 (HLB>12)	30%
	Diethyleneglycol monomethyl ether	40%

Formulation 4 (Table 2, Example 7)

	Dodecyldimethylamine	25%
10	N-Coconut alkyl-dipropylenetriamine	5%
	Acetic acid	10%
	Isopropyl alcohol	10%
	Water	50%

Formulation 5 (Table 2, Example 8)

15	N-Beef tallow alkyl-dimethylamine	5%
	N-Dodecyl-tripropylenetetraamine	25%
	Lactic acid	23%
	Toxanon P-900	7%
	Diethyleneglycol monomethyl ether	40%

20 Formulation 6 (Table 2, Example 9)

	N-Oleyl-propylenediamine	10%
	Didodecylmethylamine	10%
	N-Coconut alkyl-dipropylenetriamine	4%
	Acetic acid	2%
25	Toxanon P-900	18%

Diethyleneglycol monomethyl ether 56%

Formulation 7 (Table 2, Example 10)

N-Beef tallow alkyl-N,N-bis(3-aminopropyl)amine 10%
 Soybean alkyldimethylamine 3%
 5 N-Octadecyl-tripropylene tetraamine 10%
 Toxanon P-900 25%
 Diethylene glycol monomethyl ether 52%

Formulation Example 8 (Table 3, Comparative Example 2)

10 N-Beef tallow alkyl-N,N-bis(3-aminopropyl)amine 20%
 Toxanon P-900 20%
 Diethyleneglycol monomethyl ether 60%

Test Example 1

(Test on preventive effects against adhesion in a seawater system)

15 Seawater was pumped with a submersible pump from a seawater conduit in an iron manufacturing factory where serpulidae, caused a lot of trouble, and was passed in one direction through model passageways of PVC (polyvinyl chloride) tube with inner diameters of 65mm and lengths of 2m with
 20 test nets put therein (at a flow rate of 2 tons/hour) for 40 days in the adhering season of serpulidae. Into the passageways, each the formulation prepared, as the above mentioned were poured with chemical pumps. Then the number of serpulidae and other organisms which adhered was counted.

The injected chemicals and are shown in Tables 1 to 4
 (Tables 1 and 3 are the results testing from June to August
 in 1994 and Tables 2 and 4 are the results testing from June
 to August in 1995), wherein the following symbols denote
 5 respective chemicals:

(1) Compounds of the sub-formula (I')

- I'-a : N-Dodecyl-propylenediamine
- I'-b : N-Hexadecyl-propylenediamine
- I'-c : N-Octadecyl-propylenediamine
- 10 I'-d : N-Oleyl-propylenediamine
- I'-e : N-Coconut alkyl-propylenediamine
- I'-f : N-Beef tallow alkyl-propylenediamine
- I'-g : N-Hardened beef tallow alkyl-propylenediamine
- I'-h : N-Beef tallow alkyl-N,N-bis(3-aminopropyl)amine
- 15 I'-i : N-Hardened beef tallow alkyl-N,N-bis
 (3-aminopropyl)amine
- I'-j : N-Soybean alkyl-N,N-bis(3-aminopropyl)amine
- I'-k : N-Oleyl-N,N-bis(3-aminopropyl)amine

(2) Compounds of the sub-formula (I'')

- 20 I''-a : Dodecyldimethylamine
- I''-b : Oleyldimethylamine
- I''-c : Soybean alkyl dimethylamine
- I''-d : Beef tallow alkyl dimethylamine
- I''-e : Didodecylmethylamine

I"-f : Tetradecylhexadecylmethylanine

(3) Compounds of the formula (II)

II-a : N-Octadecyl-dipropylenetriamine

II-b : N-Coconut alkyl-dipropylenetriamine

5 II-c : N-Dodecyl-tripropylenetetraamine

II-d : N-Octadecyl-tripropylenetetraamine

II-e : N-Oleyl-tripropylenetetraamine

II-f : N-Beef tallow alkyl-tripropylenetetraamine

II-g : N-Beef tallow alkyl-tetrapropylenepentaamine

10 II-h : N-Tetradecyl-tetrapropylenepentaamine

II-i : N-Hexadecyl-tripropylenetetraamine

II-j : N-Beef tallow alkyl-dipropylenetriamine

(4) Other component

III-a : Zinc dimethyldithiocarbamate

Table 1

		Compound •Salt	Concen- tra- tion (mg/l)	Dosing Time (Hr)	Ratio	Serpulidae		Barnacles		Green Mussels		Tubularia
						Adhered number (number /m ²)	Mean length of tube (mm)	Adhered number (number /m ²)	Mean major axis of base (mm)	Adhered number (number /m ²)	Mean length of shell (mm)	coverage (%)
Examples	1	I'-e •hydro- chloride	0.01	24	1.0	0	-	300	< 1	0	-	0
		II-f •hydro- chloride	0.01		1.0							
	2	I'-f	0.02	24	1.0	0	-	200	< 1	0	-	0
			II-e •acetate		0.004	0.2						
	3	I'-b	0.03	18	1.0	0	-	300	< 1	0	-	0
			II-a		0.015	0.5						
	4	I'-h	0.005	14	1.0	0	-	500	< 1	0	-	0
			II-c •lactate		0.04	8.0						
	5	I'-c •citrate	0.005	24	1.0	0	-	100	< 1	0	-	0
			II-b		0.025	5.0						
	6	I'-d	0.005	24	1.0	0	-	200	< 1	0	-	0
			II-g		0.02	4.0						

Table 2

	Compound • Salt	Concentration (mg/l)	Dosing Time (Hr)	Ratio	Serpulidae		Barnacles		Green Mussels		Tubularia
					Adhered number (number /m ²)	Mean length of tube (mm)	Adhered number (number /m ²)	Mean major axis of base (mm)	Adhered number (number /m ²)	Mean length of shell (mm)	coverage (%)
Examples	7	I"-a • acetate	0.05	1.0	0	-	50	< 1	0	-	0
		II-b • acetate	0.01	0.2							
	8	I"-d	0.008	1.0	0	-	10	< 1	0	-	0
		II-c • lactate	0.04	5.0							
	9	I'-d	0.04	1.0							
		I"-e • acetate	0.04	1.0	0	-	20	< 1	0	-	0
		II-b	0.016	0.4							
	10	I'-h	0.02	1.0							
		I"-c	0.006	0.3	0	-	10	< 1	0	-	0
		II-d	0.02	1.0							
	11	I'-a • hydro- chloride	0.006	1.0							
		I"-b	0.03	5.0	0	-	10	< 1	0	-	0
		II-h • citrate	0.03	5.0							

Table 3

		Compound •Salt	Concen- tra- tion (mg/l)	Dosing Time (Hr)	Serpulidae		Barnacles		Green Mussels		Tubularia
					Adhered number (number /m ²)	Mean length of tube (mm)	Adhered number (number /m ²)	Mean major axis of base (mm)	Adhered number (number /m ²)	Mean length of shell (mm)	coverage (%)
Comparative Examples	1	I'-f •hydro- chloride	0.08	24	28000	10	1500	1	1500	1	10
	2	I'-h	0.10	18	25000	11	5000	2	3000	1	15
	3	II-b •acetate	0.06	24	12000	10	3000	2	2000	1	10
	4	II-e	0.04	14	15000	10	3000	< 1	2000	1	15
	5	II-g	0.06	24	17000	10	4000	2	2000	1	15
	6	Untreated	-	-	58000	14	43000	9	32000	8	45

Table 4

		Compound • Salt	Concentration (mg/l)	Dosing Time (Hr)	Serpulidae		Barnacles		Green Mussels		Tubularia coverage (%)
					Adhered number (number /m ²)	Mean length of tube (mm)	Adhered number (number /m ²)	Mean major axis of base (mm)	Adhered number (number /m ²)	Mean length of shell (mm)	
Comparative Examples	7	I"-a •hydro- chloride	2.0	16	18000	12	200	4	900	1	15
	8	I"-b	1.0	18	15000	12	100	1	500	1	5
	9	I"-c	0.5	20	6000	10	100	1	1000	1	20
	10	I"-d	0.05	24	2000	13	50	1	700	1	5
	11	I"-e •acetate	0.08	24	5000	10	50	1	900	1	5
	12	I'-d	1.0	18	13000	13	1500	3	2000	1	20
	13	II-d •hydro- chloride	0.5	24	10000	12	1200	2	1500	1	15
	14	Untreated	-	-	62000	14	35000	11	26000	9	40

Consideration

From the above test results, combined use of the compound of the sub-formular (I') and/or the compound of the sub-formula (I'') with the compound of the formula (II) was found to have a synergistic effect (see Ex. Nos. 1 to 11) against prevention of serpulidae adhesion, while single use of the individual compound did not exhibit effects against serpulidae (see Comp. Ex. Nos. 1 to 14).

Test Example 2

(Test on preventive effects against adhesion to fishing nets)

Culture nets made of polyethylene (100 strings, 5 knots, 40cm x 60cm) were used as test nets. Antifouling agents for fishing nets were prepared at the mixing ratios shown in Table 5 to 7. The test nets were dipped into each of the antifouling agents to allow the agents to stick thereto, and then air-dried for 3 days. The test nets were then hung at a depth of 1.0 to 1.5m from the surface of the sea from raft in Houzaura Bay, Mie Prefecture, Japan for 3 months from May through July. At the end of the period, the antifouling effects against serpulidae and other adherent organisms were observed. The results are shown in Table 8, wherein shown are the weight (wet weight) of adhering organisms and percentage by weight of the individual adhering organisms.

Table 5

		Compound •Salt	Ratio of solid content	Ratio	Mixing Ratio (parts by weight)								
					Diethyl phthal- ate	Liquid par- affin	Acrylic resin	Poly- butene	Rosin resin	Couma- rone resin	PGM *	Xylene	Sum
Examples	1'	I'-b •hydro- chloride	10.0	1.0	5		10		10		10	45	100
		II-j •hydro- chloride	10.0	1.0									
	2'	I'-f	2.3	1.0		10	5	5	5	5	20	30	100
		II-c •acetate	17.7	7.7									
	3'	I'-e	16.7	1.0		5	10		5	5		55	100
		II-i	3.3	0.2									
	4'	I'-h	6.7	1.0	5	5	10	5	5		15	35	100
		II-b •citrate	13.3	2.0									
	5'	I'-d •acetate	4.0	1.0	5		10	5		5	10	45	100
		II-j	16.0	4.0									

*PGM: propyleneglycol monomethylether

Table 6

		Compound •Salt	Ratio of solid content	Ratio	Mixing Ratio (parts by weight)								
					Diocetyl phthal- ate	Liquid par- affin	Acrylic resin	Poly- butene	Rosin resin	Couma- rone resin	PGM *	Xylene	Sum
Examples	6'	I'-e	5.0	1.0	5		10	5	5	5	5	45	100
		II-g •acetate	15.0	3.0									
	7'	I'-g	7.5	1.0	5	5	5	5	10		55	100	
		II-e	7.5	1.0									
		III-a	5.0										
	8'	I"-a •hydro- chloride	10.0	1.0		5	10		5	5		55	100
		II-a •hydro- chloride	10.0	1.0									
	9'	I'-j	10.0	1.0		10	5	5	5		15	40	100
		I"-b •acetate	5.0	0.5									
		II-f	5.0	0.5									
	10'	I'-a •hydro- chloride	6.0	1.0	5		10	5		5	10	45	100
		I"-f •acetate	9.0	1.5									
		II-h •hydro- chloride	5.0	0.8									

*PGM: propyleneglycol monomethylether

Table 7

	Compound •Salt	Ratio of solid content	Mixing Ratio (parts by weight)								
			Diethyl phthalate	Liquid paraffin	Acrylic resin	Polybutene	Rosin resin	Coumarone resin	PGM *	Xylene	Sum
Comparative Examples	1' I'-b •acetate	20.0	5		10	5	5		10	45	100
	2' I'-g	20.0	5	5	5	5	5	5		50	100
	3' I'-h	20.0	5		10		5	5		55	100
	4' II-j	20.0		10		5	10	5	5	45	100
	5' II-b •hydrochloride	20.0	5		10		5	5	10	45	100
	6' II-e	20.0	5		10	5		5		55	100
	7' II-g •acetate	20.0		10		5	10	5	5	45	100
	8' I"-a	20.0	5		10	5		5		55	100
	9' I"-f •hydrochloride	20.0	5		10	5	10		5	45	100
	10' Untreated	-	-	-	-	-	-	-	-	-	-

*PGM: propyleneglycol monomethylether

Table 8

		Adhering organisms after 3 months: percentage (%)				Wet weight (g) of adhering matters after 3 months
		Serpulidae	Barnacles	Blue Mussels	Polyzoa	
Examples	1'	0	0	0	0	10
	2'	0	0	0	0	10
	3'	0	0	0	0	10
	4'	0	0	0	0	10
	5'	0	0	0	0	10
	6'	0	0	0	0	10
	7'	0	0	0	0	10
	8'	0	0	0	0	10
	9'	0	0	0	0	10
	10'	0	0	0	0	10
Comparative Examples	1'	60	20	0	20	520
	2'	70	20	0	10	400
	3'	40	30	10	20	600
	4'	60	20	0	20	450
	5'	50	30	10	10	550
	6'	60	10	0	30	390
	7'	60	20	5	15	500
	8'	60	20	10	10	400
	9'	70	10	10	10	430
	10'	60	10	10	20	2300

Consideration

From the above test results, it was found that the antifouling agents for fishing nets of the invention prepared by mixing the compound of the sub-formula (I') and/or the compound of the sub-formula (I'') with the compound of the formula (II) exhibited antifouling effects against serpulidae for a long time more than 3 months (see Ex. Nos. 1' to 10'), while single use of the individual compound did not exhibit long-term effects (see Comp. Ex. Nos. 1 to 10').

Test Example 3

(Test on antifouling effects as antifouling coating)

Rigid PVC boards of 7cm x 20cm were used as test boards. Antifouling paints were prepared at the mixing ratios shown in Table 9 to 11. Each paint was applied twice to the board in an amount from 1.5 to 2.0kg/m². The test boards were then hung at a depth of 1.0 to 1.5m from the surface of the sea from raft in Houzaura Bay, Mie Prefecture, Japan for a year from May. After 6 months and 12 months from the hanging, the antifouling effect against serpulidae and other adherent organisms was observed. The results are shown in Tables 12 and 13, wherein shown are the weight (wet weight) of adhering organisms and percentage by weight of individual adhering organisms.

Table 9

		Compound • Salt	Ratio of solid content	Ratio	Mixing Ratio (parts by weight)												Sum
					Talc	Titanium white	Phthalocyanine-B	Red oxide	Diethyl phthalate	Liquid paraffin	Acrylic resin	Polybutene	Rosin resin	Coumarone resin	PGM *	Xylene	
Examples	1"	I'-b•hydrochloride	10.0	1.0		10		10	8		10	5	5		7	25	100
		II-j•hydrochloride	10.0	1.0													
	2"	I'-f	2.3	1.0													
		II-c •acetate	17.7	7.7	5	15	5			8	10		5	5	5	22	100
	3"	I'-e	16.7	1.0		20	3		7			5	10	5		30	100
		II-i	3.3	0.2													
	4"	I'-h	6.7	1.0		5		15	6		10		10			34	100
		II-b •citrate	13.3	2.0													
	5"	I'-d •acetate	4.0	1.0													
		II-j	16.0	4.0	10	10	3			8	10	5		5	5	24	100
	6"	I'-k	16.0	1.0													
		II-g	4.0	0.25	3	5	5	10	8		10	5	5	5		24	100

*PGM: propyleneglycol monomethylether

Table 10

		Compound •Salt	Ratio of solid con- tent	Ratio	Mixing Ratio (parts by weight)												Sum
					Talc	Tita- nium white	Phtha- locya- nine-B	Red ox- ide	Diethyl phthal- ate	Liquid par- affin	Acryl- ic resin	Poly- bu- tene	Rosin resin	Couma- rone resin	PGM *	Xy- lene	
Examples	7"	I'-g	7.5	1.0													
		II-e	7.5	1.0		10		10	3	7	10	10			5	30	100
		III-a	5.0														
	8"	I"-a•hydro- chloride	10.0	1.0		10		10	7		15		5	5		28	100
		II-a•hydro- chloride	10.0	1.0													
	9"	I'-j	10.0	1.0													
		I"-b•acetate	5.0	0.5	5	15				10	10	10			5	25	100
		II-f	5.0	0.5													
	10"	I'-a•hydro- chloride	6.0	1.0													
		I"-f•acetate	9.0	1.5		15	3		7		10		10			35	100
		II-h•hydro- chloride	5.0	0.8													

*PGM: propyleneglycol monomethylether

Table 11

		Compound •Salt	Ratio of solid con- tent	Mixing Ratio (parts by weight)												Sum
				Talc	Tita- nium white	Phtha- locya- nine-B	Red ox- ide	Diethyl phthal- ate	Liquid par- affin	Acryl- ic resin	Poly- bu- tene	Rosin resin	Couma- rone resin	PGM *	Xy- lene	
Comparative Examples	1"	I'-b•acetate	20.0	5	15	3		6		10	5	5		5	26	100
	2"	I'-g	20.0		7		13	8			5	10		7	30	100
	3"	I'-h	20.0	5	12	3			6	5	5	5	5		34	100
	4"	II-j	20.0		5		15		8	10			10		32	100
	5"	II-b•hydro- chloride	20.0	8	13			7		5	5	5	5	2	30	100
	6"	II-e	20.0		18	3			7		10	5	5		32	100
	7"	II-g	20.0		10		10	5		5	5		10		35	100
	8"	I"-a	20.0		8		12	7			10	8			35	100
	9"	I"-f•hydro- chloride	20.0	5	13				7	5	3	5	7		35	100
	10"	Untreated	-	-	-	-	-	-	-	-	-	-	-	-	-	-

*PGM: propyleneglycol monomethylether

Table 12

		All adhering organisms after 6 months/all adhered area (%)	Adhering organisms after 6 months: Adhered area (%)				All adhering organisms after 12 months/all adhered area (%)	Adhering organisms after 12 months: Adhered area (%)			
			Serpu- lidae	Barna- cles	Bivalves	Poly- zoa		Serpu- lidae	Barna- cles	Bivalves	Poly- zoa
Examples	1"	0	0	0	0	0	25	0	10	0	15
	2"	0	0	0	0	0	20	0	5	5	10
	3"	0	0	0	0	0	20	0	0	10	10
	4"	0	0	0	0	0	25	0	10	5	10
	5"	0	0	0	0	0	20	0	0	10	10
	6"	0	0	0	0	0	20	0	5	5	10
	7"	0	0	0	0	0	20	0	10	0	10
	8"	0	0	0	0	0	20	0	5	0	15
	9"	0	0	0	0	0	20	0	5	5	10
	10"	0	0	0	0	0	20	0	10	0	10

Table 13

		All adhering organism after 6 months/all adhered area (%)	Adhering organisms after 6 months: Adhered area (%)				All adhering organism after 12 months/all adhered area (%)	Adhering organisms after 12 months: Adhered area (%)			
			Serpu- lidae	Barna- cles	Bivalves	Poly- zoa		Serpu- lidae	Barna- cles	Bivalves	Poly- zoa
Comparative Examples	1"	50	30	10	0	10	100	50	20	10	20
	2"	60	40	0	10	10	100	60	10	10	20
	3"	60	20	20	10	10	100	45	30	10	15
	4"	40	20	0	10	10	100	50	10	25	15
	5"	50	20	0	15	15	100	50	10	15	25
	6"	40	20	0	10	10	100	45	15	15	25
	7"	60	30	10	10	10	100	55	15	15	15
	8"	50	20	10	10	10	100	45	30	5	20
	9"	60	30	20	5	5	100	50	25	10	15
	10"	100	60	20	10	10	100	40	30	10	20

Consideration

From the above test results, it was found that the antifouling agents of the invention prepared by mixing the compound of the sub-formula (I') and/or the compound of the sub-formula (I'') with the compound of the formula (II) exhibited antifouling effects against serpulidae for a long time more than 6 months (see Ex. Nos. 1" to 10"), while single use of the individual compound did not exhibit long-term effects (see Comp. Ex. Nos. 1" to 10").

The antifouling agent for cooling seawater systems and fishing nets and antifouling paint according to the invention can efficiently avoid damage caused by marine adherent organisms, especially by serpulidae, for a long time more than 12 months.



What is claimed is:

1. A preventive agent against adhesion of a marine organism comprising:

at least one amine compound represented by the following formula (I):



, wherein R is a C₈₋₂₂ saturated or unsaturated aliphatic hydrocarbon group, R¹ is hydrogen atom, aminopropyl, a C₁₋₂₂ saturated aliphatic hydrocarbon or C₂₋₂₂ unsaturated aliphatic hydrocarbon group, R² is aminopropyl, a C₁₋₈ saturated aliphatic hydrocarbon or C₂₋₈ unsaturated aliphatic hydrocarbon group, provided that R¹ is hydrogen atom or aminopropyl group when R² is aminopropyl group, or a salt thereof; and

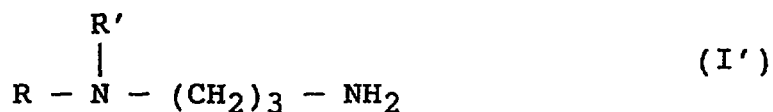
at least one N-alkyl polyamine compound represented by the following formula (II):



, wherein R is a C₈₋₂₂ saturated or unsaturated aliphatic hydrocarbon group and n is an integer from 2 to 4, or a salt thereof in an amount of 0.1 to 9 parts by weight to one part by weight of the compound (I).



2. A preventive agent against adhesion of a marine organism according to claim 1 in which the amine compound of the formula (I) is represented by the following sub-formula (I'):



, wherein R is the same as defined in the formula (I) and R' is hydrogen atom or aminopropyl group.

3. A preventive agent against adhesion of a marine organism according to claim 1 in which the amine compound of the formula (I) is represented by the following sub-formula (I''):



, wherein R is the same as defined in the formula (I); R_a is a C₁₋₂₂ saturated aliphatic hydrocarbon or C₂₋₂₂ unsaturated aliphatic hydrocarbon group, and R_b is a C₁₋₈ saturated aliphatic hydrocarbon or C₂₋₈ unsaturated aliphatic hydrocarbon group.

4. A preventive agent against adhesion of a marine organism according to claim 1 in which the amine compound of the formula (I) includes at least one compound represented by



the sub-formula (I') and at least one of the compounds represented by the sub-formula (I'') at a weight ratio from 1:10 to 10:1.

5 5. A preventive agent against adhesion of a marine organism according to claim 1 in which the C₈₋₂₂ saturated or unsaturated aliphatic hydrocarbon group represented by R is octyl, decyl, dodecyl, tetradenyl, hexadecyl, octadecyl, oleyl, coconut alkyl, beef tallow alkyl, hardened beef tallow alkyl or soybean alkyl.

10 6. A preventive agent against adhesion of a marine organism according to claim 1 in which the C₁₋₂₂ saturated aliphatic hydrocarbon group represented by R¹ is methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, coconut alkyl, beef tallow
15 alkyl, hardened beef tallow alkyl or soybean alkyl.

7. A preventive agent against adhesion of a marine organism according to claim 1 in which the C₂₋₂₂ unsaturated aliphatic hydrocarbon group represented by R¹ is myristeyl, palmiteyl, oleyl, linoleyl, coconut alkyl, beef tallow
20 alkyl, hardened beef tallow alkyl or soybean alkyl.

8. A preventive agent against adhesion of a marine organism according to claim 1 in which the amine compound of the



sub-formula (I') is N-dodecyl-propylenediamine, N-hexadecyl-propylenediamine, N-octadecyl-propylenediamine, N-oleyl-propylenediamine, N-coconut alkyl-propylenediamine, N-beef tallow alkyl-propylenediamine, N-hardened beef tallow alkyl-propylenediamine, N-beef tallow alkyl-N,N-bis(3-aminopropyl)amine, N-hardened beef tallow alkyl-N,N-bis(3-aminopropyl)amine, N-soybean alkyl-N,N-bis(3-aminopropyl)-amine or N-oleyl-N,N-bis(3-aminopropyl)amine.

9. A preventive agent against adhesion of a marine organism according to claim 1 in which the amine compound of the sub-formula (I'') is dodecyldimethylamine, oleyldimethylamine, soybean alkyl dimethylamine, beef tallow alkyl dimethylamine, didodecylmethylamine or tetradecylhexadecylmethylamine.

10. A preventive agent against adhesion of a marine organism according to claim 1 in which the amine compound (II) is N-octadecyl-dipropylenetriamine, N-coconut alkyl-dipropylenetriamine, N-dodecyl-tripropylenetetraamine, N-dodecyl-tripropylenetetraamine, N-octadecyl-tripropylenetetraamine, N-oleyl-tripropylenetetraamine, N-beef tallow alkyl-tripropylenetetraamine, N-beef tallow alkyl-tetrapropylene-pentaamine, N-tetradecyl-tetrapropylene-pentaamine, N-hexadecyl-tripropylenetetraamine or N-beef tallow alkyl-dipropylenetriamine.



11. A preventive agent against adhesion of a marine organism according to claim 1 in which the marine organism is serpulidae.

5 12. A method of preventing adhesion of a marine organism comprising a simultaneous or separate addition to an objective seawater system of at least one amine compound represented by the formula (I) as defined in claim 1 or a salt thereof and at least one N-alkyl polyamine compound represented by the formula (II) as defined in claim 1 or a salt
10 thereof at a concentration of 0.001 to 0.2mg/L of seawater as the active ingredient.