

ANTIFOULING AGENT FOR FISHNETS

The present invention relates to a heavy metal-free antifouling solution for fishnets that effectively prevents the attachment of marine fouling organisms to nets, either for use in cultivation farms or for stationary net fishery, as well as to items submerged in water such as accessories for fishnets.

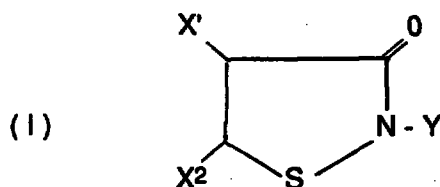
Fishnets for use in cultivation farms or in stationary net fishery and ropes used with them are submerged in seawater for a prolonged period and are prone to be infested with extensive attachments of marine fouling organisms including seaweeds, barnacles, tube worms, polyzoans and mollusks. The attachment of these marine fouling organisms prevents economical use of fishnets and costs lots of labour and money in maintenance work. It has therefore been desired to develop an antifouling agent for fishnets that remains effective and economical for a prolonged period and which is simple to use without causing pollution of the environment.

With a view to attaining this objective, various studies and proposals have been made and it is generally known that a series of organotin compounds (e.g. trialkyl or triphenyl tin compounds) are effective for practical purposes. However, most of the previously proposed organotin compounds are highly toxic and products containing them might cause damage to users if not handled carefully. They are also disadvantageous from the viewpoint of the need to prevent environmental pollution. For these reasons, the advent of a heavy metal- and pollution-free antifouling agent for fishnets has been strongly desired.

Japanese Patent Publication No. 50984/1986 shows an antifouling agent for marine structures that contains 3-isothiazolone as an effective ingredient. Japanese Patent Application (OPI) No. 34604/1981 (the term OPI as used herein means an unexamined published Japanese patent application) shows a marine antifouling agent or an antifouling solution for fishnets that employs tetrachloroisophthalonitrile. Japanese Patent Application (OPI) No. 81505/1981 shows a marine antifouling agent or an antifouling solution for fishnets that employs a dialkyl sulfide or tetraalkylthiuram disulfide compound. Japanese Patent Application (OPI) No. 118006/1981 shows a marine antifouling agent or an antifouling solution for fishnets that employs a combination of the three components mentioned above. However, these compounds, when taken individually, are not satisfactory for practical purposes since they are comparatively low in their ability to prevent attachment of marine antifouling organisms. In addition, very few of them exhibit a desired antifouling efficacy against a broad spectrum of fouling organisms. Although some of the proposals made in the above listed patents are being commercialized, there still is a need to develop an antifouling agent for fishnets that is potentially low in environmental hazard and toxicity to fish and which yet shows satisfactory results in practical applications.

In one aspect, the present invention provides an antifouling composition for fishnets comprising

(a) at least one compound of the formula (I)

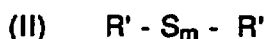


wherein Y is (C₁-C₁₈)alkyl or (C₃-C₁₂)cycloalkyl each optionally substituted with one or more of hydroxy, halo, cyano, alkylamino, dialkylamine, arylamino, carboxy, carbalkoxy, alkoxy, aryloxy, alkylthio, arylthio, haloalkoxy, cycloalkylamino, carbamoxy, or isothiazolonyl; an unsubstituted or halo-substituted (C₂-C₈)alkenyl or alkynyl; a (C₇-C₁₀)aralkyl optionally substituted with one or more of halogen, (C₁-C₄)alkyl or (C₁-C₄)alkoxy; or an aryl optionally substituted with one or more of halogen, nitro, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, phenoxy, hydroxy, trihalomethyl, (C₁-C₄)alkyl-acylamino, carb(C₁-C₄)alkoxy or sulfamyl,

and X' and X² are each independently H, (C₁-C₄)alkyl or halogen; and

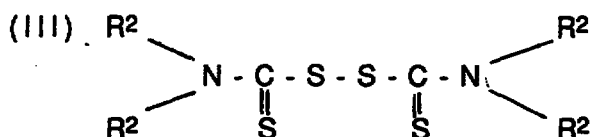
(b) one or both of

(i) at least one compound of the formula(II)



wherein each R' is independently (C₁-C₂₀)alkyl and m is an integer of from 2 to 10;

(ii) at least one compound of the formula (III)



wherein each R² is independently (C₁-C₄)alkyl.

Preferably, the antifouling composition of the invention additionally comprises tetrachloroisophthalonitrile.

The invention also provides a method of preventing or inhibiting the growth of marine fouling organisms on fishnets submerged in water, comprising incorporating onto a fishnet a composition as defined above.

According to the studies conducted by the present inventors, compounds of the general formulas (I), (II) and (III) and tetrachloroisophthalonitrile, when taken individually, are low in their ability to prevent attachment of marine antifouling organisms and hence are not satisfactory for use in practical applications. However, when the compound (I) and one or both of the compounds (II) and (III) are used in combination, or if they are combined with tetrachloroisophthalonitrile, unexpectedly high synergistic effects are exhibited and antifouling agents that contain them show balanced effects in practical applications while presenting low toxicity to fish and minimal risk of environmental pollution.

Examples of the compound represented by the general formula (I), in which it is preferred that at least one of X' and X² is halogen, include:

5-chloro-2-phenethyl-3-isothiazolone, 4-bromo-2-n-dodecyl-3-isothiazolone, 4,5-dichloro-2-n-octyl-3-isothiazolone, 4-methyl-5-chloro-2-(4'-chlorobenzyl)-3-isothiazolone, 4,5-dichloro-2-(4'-chlorobenzyl)-3-isothiazolone, 4,5-dichloro-2-(4'-chlorophenyl)-3-isothiazolone, 4,5-dichloro-2-(2'-methoxy-3'-chlorophenyl)-3-isothiazolone, 4,5-dibromo-2-(4'-chlorobenzyl)-3-isothiazolone, 4-methyl-5-chloro-2-(4'-hydroxyphenyl)-3-isothiazolone, 4,5-dichloro-2-n-hexyl-3-isothiazolone, and 5-chloro-2-(3',4'-dichlorophenyl)-3-isothiazolone. Of course, these are not the sole examples of compound (I) that can be used in the present invention.

Examples of the compound represented by the general formula (II) include: diethyl pentasulfide, dipropyl tetrasulfide, diisopropyl trisulfide, di-t-butyl ditetrasulfide, dihexyl pentasulfide, dioctyl tetrasulfide, di-t-nonyl pentasulfide,

di-t-dodecyl pentasulfide, ditetradecyl tetrasulfide, dinonadecyl tetrasulfide, and di-t-butyl decasulfide. Of course, these are not the sole examples of compound (II) that can be used in the present invention.

Examples of the compound represented by the general formula (III) include: tetraethylthiuram disulfide, tetraisopropylthiuram disulfide, and tetra-n-butylthiuram disulfide. Of course, these are not the sole examples of compound (III) that can be used in the present invention.

The antifoulant composition of the invention is customarily incorporated in a solvent such as xylene, solvent naphtha, diethylbenzene, pseudocumene, mesitylene, triethylbenzene and butyl acetate, with xylene, solvent naphtha, pseudocumene or butyl acetate being preferred.

The mixing proportions of the compound (I) and one or both of the compounds (II) and (III), and tetrachloroisophthalonitrile if this is used, and the total amount of their use are not limited to any values since these factors will vary both with the antifouling performance required of the final product and with the conditions of the environment in which it is used. Normally, these compounds and optional tetrachloroisophthalonitrile are used in amounts giving a total active ingredient concentration ranging from 3 to 30 parts, desirably from 8 to 20 parts, per 100 parts of the final product.

The mixing proportions of the compound (I) and one or both of the compounds (II) and (III) and the optional component tetrachloroisophthalonitrile can be varied in accordance with the specific conditions of the environment in which the antifouling agent of the present invention is used. Additional ingredients that are known to be effective and safe may also be incorporated and this offers the advantage that more balanced effects are anticipated against various marine fouling organisms.

The antifouling solution for fishnets of the present invention can be prepared with ease. Compound (I) and one or both of the compounds (II) and (III), and optionally tetrachloroisophthalonitrile may be dissolved in solvents such as xylene, solvent naphtha and pseudocumene together with resins such as natural resins, oily resins, synthetic resin and synthetic rubber-base resins that are employed in ordinary paints, and optional additives such as colorants and plasticizers that may be incorporated as required. Advantageous resins include polyacrylics, polybutenes, rosins, coumarone resins, polyvinyl chloride, chlorinated rubbers, alkyd resins, and ethylene/vinyl acetate copolymer resins.

The following examples are given for illustrating the formulation of the antifouling agent for fishnets of the present invention. It should however be noted that the present invention is by no means limited by these examples. In the following examples, the amounts of all ingredients incorporated are expressed in weight percent.

EXAMPLE 1

4,5-Dichloro-2-n-octyl-3-isothiazolone	5%
Tetraethylthiuram disulfide	10%
Acrylic resin (in 50% xylene solution)	20%
Xylene	65%

EXAMPLE 2

5-chloro-2-n-decyl-3-isothiazolone	5%
Di-t-nonyl pentasulfide	10%
Acrylic resin (in 50% xylene solution)	22%
Xylene	63%

EXAMPLE 3

4,5-Dichloro-2-(4'-chlorobenzyl)-3-isothiazolone	5%
Tetraethylthiuram disulfide	10%
Acrylic resin (in 50% xylene solution)	22%
Polybutene	5%
Xylene	48%
Pseudocumene	10%

EXAMPLE 4

4,5-Dichloro-2-(4'-chlorophenyl)-3-isothiazolone	3%
4-Methyl-5-chloro-2-(4'-hydroxyphenyl)-3-isothiazolone	2%
Tetraethylthiuram disulfide	10%
Acrylic resin (in 50% xylene solution)	22%
Xylene	53%
Pseudocumene	10%

EXAMPLE 5

4-Bromo-2-n-decyl-3-isothiazolone	5%
Tetraethylthiuram disulfide	6%
Di-t-dodecyl pentasulfide	6%
Acrylic resin (in 50% xylene solution)	22%
Coumarone	3%
Xylene	58%

EXAMPLE 6

4-Methyl-5-chloro-2-(4'-chlorobenzyl)-3-isothiazolone	5%
Tetraethylthiuram disulfide	6%
Di-t-nonyl pentasulfide	6%

Acrylic resin (in 50% xylene solution)	22%
Xylene	51%
Pseudocumene	10%

EXAMPLE 7

4,5-Dichloro-2-n-octyl-3-isothiazolone	3%
5-Chloro-2-phenethyl-3-isothiazolone	2%
Tetraethylthiuram disulfide	6%
Di-t-nonyl pentasulfide	6%
Acrylic resin (in 50% xylene solution)	22%
Xylene	61%

EXAMPLE 8

4,5-Dichloro-2-n-octyl-3-isothiazolone	5%
Di-t-nonyl pentasulfide	5%
Tetrachloroisophthalonitrile	5%
Acrylic resin (in 50% xylene solution)	22%
Xylene	43%
Pseudocumene	20%

EXAMPLE 9

4,5-Dichloro-2-(4'-chlorophenyl)-3-isothiazolone	5%
Di-t-nonyl pentasulfide	5%
Tetrachloroisophthalonitrile	5%
Acrylic resin (in 50% xylene solution)	22%
Xylene	43%
Pseudocumene	20%

EXAMPLE 10

4,5-Dichloro-2-(4'-chlorobenzyl)-3-isothiazolone	5%
Tetraethylthiuram disulfide	5%
Tetrachloroisophthalonitrile	5%
Acrylic resin (in 50% xylene solution)	22%
Xylene	43%
Pseudocumene	20%

EXAMPLE 11

4,5-Dichloro-2-n-hexyl-3-isothiazolone	3%
4,5-Dichloro-2-n-tridecyl-3-isothiazolone	2%
Tetraethylthiuram disulfide	5%
Tetrachloroisophthalonitrile	5%
Acrylic resin (in 50% xylene solution)	22%
Xylene	43%
Pseudocumene	20%

EXAMPLE 12

4,5-Dichloro-2-n-octyl-3-isothiazolone	5%
Di-t-nonyl pentasulfide	3%
Tetraethylthiuram disulfide	3%
Tetrachloroisophthalonitrile	5%
Acrylic resin (in 50% xylene solution)	22%
Xylene	42%
Pseudocumene	20%

The efficacy of the above-noted formulations of antifouling agent was tested in the experiment described below. As comparisons, the following formulations were also tested for their efficacy.

COMPARATIVE EXAMPLE 1

4,5-Dichloro-2-n-octyl-3-isothiazolone	15%
Acrylic resin (in 50% xylene solution)	22%
Xylene	63%

COMPARATIVE EXAMPLE 2

4,5-Dichloro-2-(4'-chlorobenzyl)-3-isothiazolone	15%
Acrylic resin (in 50% xylene solution)	22%
Xylene	63%

COMPARATIVE EXAMPLE 3

5-Chloro-2-phenethyl-3-isothiazolone	15%
Acrylic resin (in 50% xylene solution)	22%
Xylene	63%

COMPARATIVE EXAMPLE 4

4,5-Dichloro-2-n-hexyl-3-isothiazolone	5%
4,5-Dichloro-2-n-tridecyl-3-isothiazolone	10%
Acrylic resin (in 50% xylene solution)	22%
Xylene	63%

EXPERIMENT

Polyethylene fishnets (6 knots, 400 d/60 yarns) were dip-coated with the antifouling formulations prepared in Examples 1 - 12 and Comparative Examples

1 - 4. After being dried with air, the nets were submerged about 1 m below sea level in Tanabe Bay, Kii, Wakayama, Japan in early September of 1987 and held there for 4 months in order to investigate the time-dependent attachment of marine fouling organisms on the nets. The results were evaluated by the following criteria.

Rating	Attachment of fouling organisms
1	none
2	less than 1%
3	less than 5%
4	from 5% to less than 10%
5	10 - 20%
6	20 - 50%
7	more than 50%

The results are shown in Table 1 below.

TABLE 1

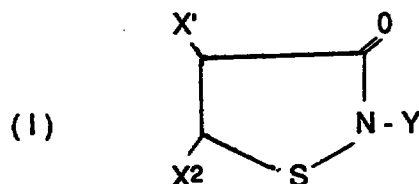
Time (month)		1	2	3	4
Formulation					
Example	1	1	2	2	3
	2	1	2	3	4
	3	1	2	2	3
	4	1	2	3	4
	5	1	2	3	4
	6	1	1	2	3
	7	1	1	2	3
	8	1	1	2	3
	9	1	1	2	3
	10	1	1	2	3
	11	1	1	2	3
	12	1	1	1	1
Comparative Example	1	4	5	7	-
	2	4	5	7	-
	3	4	5	7	-
	4	4	5	7	-
Untreated		7	-	-	-

As the data in Table 1 shows, the formulations that incorporated the compound (I) and one or both of the compounds (II) and (III), or those which contained tetrachloroisophthalonitrile in addition to these compounds provided high-performance antifouling agents for fishnets that exhibited persistent synergistic effects against attachment of marine antifouling organisms in a

CLAIMS:

1. Antifouling composition for fishnets comprising

(a) at least one compound of the formula (I)

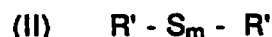


wherein Y is (C₁-C₁₈)alkyl or (C₃-C₁₂)cycloalkyl each optionally substituted with one or more of hydroxy, halo, cyano, alkylamino, dialkylamine, arylamino, carboxy, carbalkoxy, alkoxy, aryloxy, alkylthio, arylthio, haloalkoxy, cycloalkylamino, carbamoxyl, or isothiazolonyl; an unsubstituted or halo-substituted (C₂-C₈)alkenyl or alkynyl; a (C₇-C₁₀)aralkyl optionally substituted with one or more of halogen, (C₁-C₄)alkyl or (C₁-C₄)alkoxy; or an aryl optionally substituted with one or more of halogen, nitro, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, phenoxy, hydroxy, trihalomethyl, (C₁-C₄)alkyl-acylamino, carb(C₁-C₄)alkoxy or sulfamyl,

and X' and X₂ are each independently H, (C₁-C₄)alkyl or halogen; and

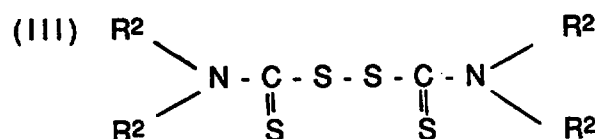
(b) one or both of

(i) at least one compound of the formula(II)



wherein each R' is independently (C₁-C₂₀)alkyl and m is an integer of from 2 to 10;

(ii) at least one compound of the formula(III)



wherein each R² is independently (C₁-C₄)alkyl.



2. Antifouling composition according to Claim 1, further comprising tetrachloroisophthalonitrile .
3. Antifouling composition according to Claim 1 or 2, wherein at least one of X' and X² in the compound of formula (I) is halogen.
4. Antifouling composition according to any preceding Claim, wherein said at least one compound of formula (I) is one or more of
5-chloro-2-phenethyl-3-isothiazolone, 4-bromo-2-n-dodecyl-3-isothiazolone, 4,5-dichloro-2-n-octyl-3-isothiazolone, 4-methyl-5-chloro-2-(4'-chlorobenzyl)-3-isothiazolone, 4,5-dichloro-2-(4'-chloro-benzyl)-3-isothiazolone, 4,5-dichloro-2-(4'-chlorophenyl)-3-isothiazolone, 4,5-dichloro-2-(2'-methoxy-3'-chlorophenyl)-3-isothiazolone, 4,5-dibromo-2-(4'-chlorobenzyl)-3-isothiazolone, 4-methyl-5-chloro-2-(4'-hydroxyphenyl)-3-isothiazolone, 4,5-dichloro-2-n-hexyl-3-isothiazolone, or 5-chloro-2-(3',4'-dichlorophenyl)-3-isothiazolone.
5. Antifouling composition according to any preceding Claim, wherein said at least one compound of formula (II) is one or more of diethyl pentasulfide, dipropyl tetrasulfide, diisopropyl trisulfide, di-t-butyl ditetrasulfide, dihexyl pentasulfide, dioctyl tetrasulfide, di-t-nonyl pentasulfide, di-t-dodecyl pentasulfide, ditetradecyl tetrasulfide, dinonadecyl tetrasulfide, and di-t-butyl decasulfide.
6. Antifouling composition according to any preceding Claim wherein said at least one compound of the formula (III) is one or more of tetraethylthiuram disulfide, tetraisopropylthiuram disulfide, and tetra-n-butylthiuram disulfide.
7. Antifouling composition according to any preceding Claim further comprising a solvent which is one or more of xylene, solvent naphtha, diethylbenzene, pseudocumene, mesitylene, triethylbenzene and butyl acetate.
8. Antifouling composition according to any preceding Claim wherein the total amount of the compounds of formulae (I), (II) and/or (III) and, if present, tetrachloroisophthalonitrile, in the composition is from 3 to 30 parts by weight.
based on 100 parts by weight of the composition.



9. Antifouling composition according to Claim 8 wherein the total amount of the compounds of formulae (I), (II) and/or (III) and, if present, tetrachloroisophthalonitrile, in the composition is from 8 to 20 parts by weight based on 100 parts by weight of the composition.

10. A method of preventing or inhibiting the growth of marine fouling organisms on fishnets submerged in water, comprising incorporating onto a fishnet a composition according to any preceding Claim.

11. Antifouling composition for fishnets comprising an isothiazolone, a compound of the formula (II) and a compound of the formula (III) and optionally tetrachloroisophthalonitrile, substantially as hereinbefore described.
