

Description

The present invention concerns antialgal compositions, methods of controlling algae, and coating compositions comprising the antialgal compositions.

The presence of algae in various aqueous systems such as latices, paints, coatings, cooling water systems, decorative ponds and the like, can cause deterioration or disfigurement of these systems. For example, painted surfaces may be disfigured by the unsightly buildup of algae, thus detracting from the overall aesthetics of the painted article; cooling towers may lose efficiency due to the buildup of algae on surfaces, thus reducing the heat transfer capabilities of the tower. It is conventional to practice methods which inhibit the algal deterioration of such systems by incorporating a variety of additives or combination of additives that are characterized by having antialgal activity.

A wide variety of materials have been used to control algae in different environments, some of which are: chlorine/bromine compounds, glutaraldehyde, isothiazolones, organotin formulations, copper salts, quaternary ammonium compounds (SD Strauss and PR Puckorius in *J. Power*, S1, June 1984), and triazines. Each has deficiencies related to toxicity, pH and temperature sensitivity, limited effectiveness, chemical stability, and/or compatibility.

Different diphenylethers ("DPEs") have been found to have widely different antimicrobial properties. See, for example, halogenated hydroxy (acyloxy) DPEs (US -A-3506720, 3629477, 4268693, 4339462), substituted nitro/halo DPEs (US- A-3772445, 3908019), and nitro/trifluoromethyl DPEs (US 4112002).

U.S.-A-3787217 and Japanese Kokai Patent Application 48-48624 to Nitta *et al* are directed towards the use of halogenated and alkyl substituted DPEs as paint antifouling agents and disclose the use of these materials to control growth of clams, barnacles, and shellfish larvae at 0.5-1.0 ppm dosage levels. These patents do not, however, teach or suggest the use or efficacy of substituted fluoroalkyl DPEs.

GB-A-1592011 to Ciba-Geigy discloses the use of DPEs containing amino (or substituted amino) or hydroxy (or ester derivatives of organic/inorganic acids) substituents as algicides, particularly dichloro and trichloro-substituted DPEs. This patent does not, however, teach or suggest the use of fluoroalkyl DPEs without hydroxy or amino substituents.

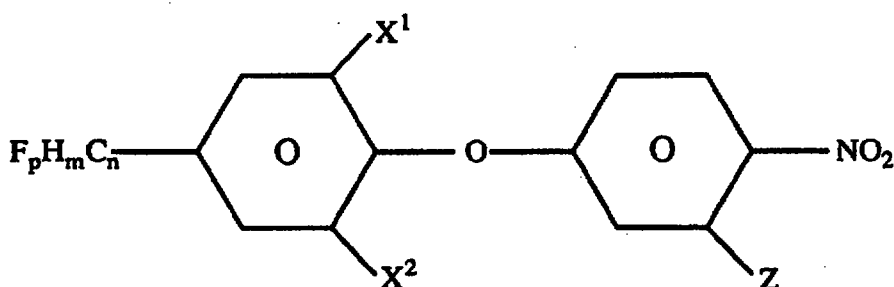
On the other hand, J. Lorenz discloses that acifluorfen (2-chloro-4-trifluoromethylphenyl-3'-carboxy-4'-nitrophenylether, sodium salt) is ineffective at all levels tested on 10 different types of algae in a screening study of commercial herbicides for use as additives in antifouling paints ("Selective Acting Antifouling Additives," Seventh Annual Congress on Marine Corrosion and Fouling, Valencia, Spain, November 10, 1988).

Numerous agricultural herbicides are known to be effective in controlling specific nuisance plants (weeds), crops, etc. The modes of action of such agricultural herbicides have been extensively studied and reported in the following references: Boger *et al* (*Z. Naturforsch*, 42c, 819(1987), 36c, 633 (1981), 39c, 486(1984), 38c, 556(1983); *Weed Science*, 33,766 (1985), 31,338 (1983), 29,371 (1981), 29,169(1981); *J Agric Food Chem*, 32,868 (1984), 32,725 (1984), 32,523 (1984); *Pesticide Biochemistry and Physiology*, 20,183 (1983), 19,309 (1983); *IUPAC Pesticide Chemistry*, Vol 3,97-102(1983), Vol 1,321-326 (1983); *Plant Science Letters*, 24,347 (1982). These articles report studies on the primary modes of action using a model alga, *Scenedesmus acutus*, to provide quick and reliable measures for understanding structure-reactivity relationships among major known herbicides, including a variety of DPEs. Boger *et al* observed the effect of many DPEs against various physiological and biochemical processes, concluding that it was not clear which structures are necessary to affect various modes of herbicidal action: inhibition of photosynthetic electron transport, energy transfer inhibition, and peroxidative destruction of photosynthetic membranes. The parameters measured in the mode of action studies were pigment loss (bleaching effects), short-chain hydrocarbon production due to fatty acid oxidation, reduction of photosynthetic oxygen evolution, etc. Thus, Boger *et al* taught that phytotoxic effects are due to the influence of more than a single biochemical mode of action. Structurally different DPEs brought about similar responses among the parameters studied by Boger *et al*. The relative potential of given DPEs or other herbicides to alter electron transport, peroxidation, or energy transfer modes of action is not necessarily indicative of herbicidal effectiveness. In summary, although Boger *et al* disclose possible pathways for herbicidal modes of action, they do not teach or suggest the use of any of these DPEs to control algae in their natural environment where water solubility, alkaline pH stability characteristics, etc., are important variables. The algae used in the Boger *et al* studies served only as a model to illustrate different biochemical modes of action operable with a variety of known herbicides.

Based on the aforementioned performance deficiencies of conventional antialgal compounds there is a need for more effective antialgal agents that can be used at lower dosage rates, thus being more cost effective for the end user, reducing the pollution load on the affected environmental systems, and reducing the side effects to nearby non-target organisms, such as fish, useful crops, etc.

In one aspect the present invention provides an antialgal composition comprising

(A) a compound of the formula



wherein

X^1, X^2 are each independently hydrogen, halogen, trihalomethyl, cyano, or $(C_1 - C_4)$ alkyl, and
 Z is hydrogen, halogen, cyano, carboxy or salt thereof, lower alkylthio, lower carbalkoxy, lower carboxyalkyl, lower carbalkoxyalkyl, lower carbalkoxyalkoxycarbonyl, lower carbalkoxyalkoxy, lower alkoxy, lower cycloalkoxy, lower alkenyl, lower alkyl, lower cycloalkyl, unsubstituted or substituted amino, or R^2O in which R^2 represents a hydrogen atom or the ester bonded acid radical of an inorganic or organic oxyacid;

p is an integer from 1 to $2n+1$;

m is an integer of 0 to $2n$;

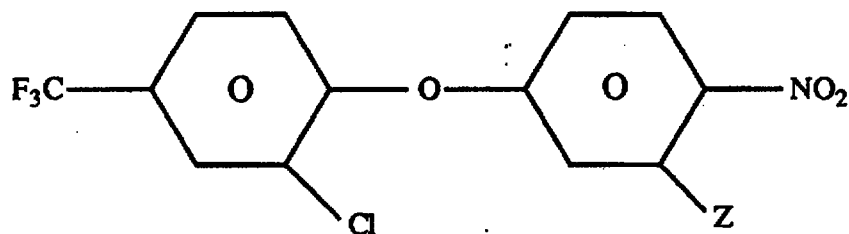
where

n is an integer of 1 to 5 and $m+p = 2n+1$;

and (B) a 3-isothiazolone.

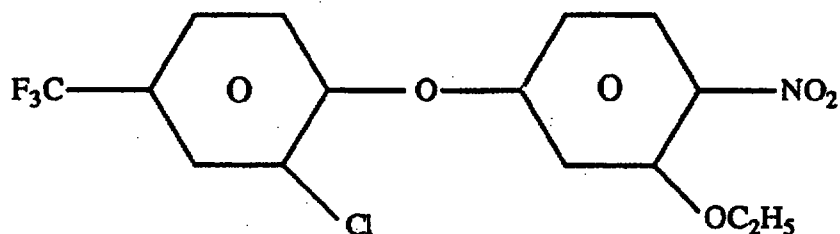
Although Z can be as defined in U.S. -A-4,772,744 and 3,798,276, preferred are compositions wherein said compound (A) has no substituents selected from the group consisting of unsubstituted or substituted amino, R^2O in which R^2 represents a hydrogen atom or the ester bonded acid radical of an inorganic or organic oxyacid, as are required by the aforementioned Ciba-Geigy reference.

More preferred are compositions wherein said compound (A) is of the formula

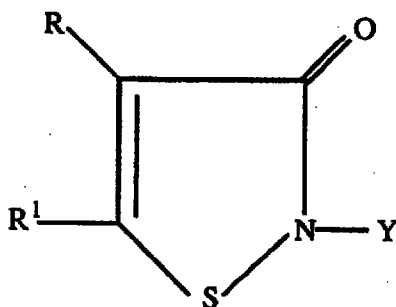


wherein Z is alkoxy, carboxy or salt thereof, carbalkoxyalkoxy, or $-CO_2CH_2CO_2C_2H_5$.

The most preferred embodiment of compound (A) is oxyfluorfen which has the formula



The preferred 3-isothiazolones are of the formula



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, carbamoy, or isothiazolonyl; an unsubstituted or halo-substituted (C₂₋₈)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)alkylacylamino, carb(C₁-C₄)alkoxy or sulfamyl;

R is hydrogen, halo, or a (C₁-C₄)alkyl; and

R¹ is hydrogen, halo or (C₁-C₄)alkyl.

Preferably, said Y is methyl, ethyl, propyl, isopropyl, butyl, hexyl, octyl, cyclohexyl, benzyl, 3,4-dichlorobenzyl, 4-methoxybenzyl, 4-chlorobenzyl, hydroxymethyl, 3,4-dichlorophenyl, 4-methoxyphenyl, 4-chlorophenyl, chloromethyl, phenethyl, 2-(4-chlorophenyl)ethyl, chloropropyl, or hydrogen.

The most preferred isothiazolones are 4,5-dichloro-2-octyl-3-isothiazolone, 2-octyl-3-isothiazolone, 5-chloro-2-methyl-3-isothiazolone, and 2-methyl-3-isothiazolone. Other isothiazolones which are preferred are as above wherein Y is (C₁-C₁₈) alkyl, (C₃-C₁₂) cycloalkyl, (C₇-C₁₀) aralkyl, or (C₇-C₁₀) ring-chlorinated aralkyl; R is hydrogen, methyl or chloro; and R¹ is hydrogen or chloro.

In another aspect, the invention provides a method of inhibiting or preventing the growth of algae in a locus subject or susceptible to contamination thereby, comprising incorporating into or onto the locus a composition according to the first aspect of the invention in an amount effective to adversely affect the growth of said algae. Typical loci to which the present invention is particularly applicable are cooling tower water and coating or impregnant compositions.

An especially useful aspect of the invention is in controlling algae in cooling tower water; preferably a concentration of from about 0.005 to about 20 ppm of the algicidal composition is maintained in the cooling tower water, more preferably a concentration of about 0.1 to 10 ppm, and most preferably a concentration of about 0.2 to 2 ppm.

Another important utility is in imparting algal resistance to a coating or impregnant composition. The composition of the invention is incorporated in a coating or impregnant at a concentration preferably of about 0.1 ppm to about 2 percent, more preferably at concentration of about 1 ppm to 1 percent, and most preferably at a concentration of about 10 to 4000 ppm.

In a marine antifoulant composition, on the other hand, the composition of the invention comprises about 1 to 10 percent of the antifoulant composition.

The algal resistant compositions can also be used in construction products such as stucco, roof mastics, wall mastics, and masonry coatings for algae protection; in clear finishes and coatings to protect underlying substrates from algae; for algae control in aquaculture, including aquaria, fish hatcheries, shrimp ponds, finfish ponds, mollusc and crustacean cultivation; for algae control in recreational and decorative bodies of water such as swimming pools, lakes, fountains and decorative ponds; for algae control in bodies of water for industrial or municipal use, such as settling or separation ponds, waste treatment ponds, and water reservoirs; for algae control in hydroponic farming; for algae control in processing and manufacture of pulp and paper products; for inclusion in plastics or in coatings for plastics to protect against algae; and in plastics or coatings for plastics for swimming pool liners.

The invention permits antialgal protection with a reduced degree of objectionable by-product odours, discolouration, and other detrimental effects on the treated systems, with compositions which are compatible with a variety of systems subject to deterioration by algae.

We prefer algicidal compositions wherein the weight ratio of (A) to (B) is from about 0.1 to 100 to about 100 to 0.1.

Recent advances in molecular biology and taxonomy have provided for the distinction of photosynthetic

procaryotic bacteria versus eucaryotic algae. In the past literature, the term "blue-green algae" made reference to a group of microorganisms which possessed chlorophyll and appeared blue-green in color. More recent textbooks on microbiology (*Biology of Microorganisms*, TD Brock, DW Smith, and MT Madigan, Prentice Hall, Inc 1984) have distinguished these organisms from eucaryotic algae, such as the green algae, and considered them to be most appropriately classified as "blue-green bacteria" or "cyanobacteria". This distinction is made since the cell architecture more closely resembles the procaryotic bacteria than eucaryotic algae. Therefore, we refer herein to photosynthetic blue-green microorganisms as cyanobacteria or blue-green bacteria.

The following examples represent just a few of the many uses and compounds of the invention. They are intended to be illustrative but not limiting. Various modifications, alternatives, and improvements should become apparent to those skilled in the art.

EXAMPLES

A. General Procedure

MIC values represent the Minimum Inhibitory Concentration. This is defined as the lowest level of compound required to completely inhibit (repress) the growth of a given organism.

A synergistic effect is defined as the response of two variables which is greater than the sum of both parts alone. Synergy was determined from combination studies with two compounds by the method of calculation described by F. C. Kull, P. C. Elsmann, H. D. Sylwestrowicz and R. K. Mayer, *Applied Microbiology* 9,538 (1961):

$$\frac{Q_A}{Q_a} + \frac{Q_B}{Q_b} = \text{synergism index (SI)}$$

where:

Q_a = quantity of compound A, acting alone, producing an end point (MIC)

Q_A = quantity of compound A, in mixture, producing an end point (MIC)

Q_b = quantity of compound B, acting alone, producing an end point (MIC)

Q_B = quantity of compound B, in mixture, producing an end point (MIC)

The following SI values may be attained:

SI > 1 represents antagonistic effect,

SI = 1 represents additive effect,

SI < 1 represents synergy.

Efficacy studies were conducted on a variety of microorganisms with oxyfluorfen and isothiazolone mixtures. The MIC studies were conducted using microtiter plate assays. In this method, a wide range of concentrations was tested by preparing two-fold serial dilutions of the compound in 96-well plastic microtiter plates. All liquid media transfers were performed with calibrated single or multichannel digital pipetters. Stock solutions of compounds were prepared in appropriate solvents and dispensed to the growth medium. All subsequent dilutions in plates were made using the desired growth medium; total volume of liquid in each well was 100 μ l. Each plate contained a concentration of both compounds made by serially titrating equal volumes of liquids in two directions in the microtiter plate. Each plate contained a control row for each combination (one component only), hence, the individual compound MIC values were also determined.

The pure cultures used in this study were obtained from the Culture Collection of Algae at the University of Texas at Austin (UTEX). Microorganisms used as inocula were cultured in shaken liquid culture (Bristol's medium, pH 7.0, 25°C, *Journal of Phycology*, 23s, 1-47, 1987 or Modified Allen's Media Formulation, described below) for one week or as needed to attain a desired cell mass. The cultures were then inoculated into the microtiter plates using a 96-prong multiple inoculator (5 μ l inoculum); each well received a standard suspension of biomass (5% inoculum). Plates were incubated at 25°C under constant illumination (500 ft candles). The extent of growth was determined under low magnification with the aid of microtiter plate reader. Growth in each cell was monitored periodically and growth/no-growth was recorded after 14 or 21 days. Results of each study were evaluated by calculating synergy index values (SI, previously described).

B. Preparation of Modified Allen's Media Formulation (pH 6.3)**Component Concentration (mg/l)**

5	NaNO ₃	250
	CaCl ₂ (2H ₂ O)	31
	MgSO ₄ (7H ₂ O)	75
10	NaCl	25
	KH ₂ PO ₄	175
	K ₂ HPO ₄	75
15	FeCl ₃ (6H ₂ O)	7.5
	Na ₂ (EDTA)	10.3
20	Na ₂ B ₄ O ₇ (10H ₂ O)	2.25
	MnCl ₂ (4H ₂ O)	0.90
	ZnCl ₂ (7H ₂ O)	0.11
25	CuCl ₂ (2H ₂ O)	0.025
	Na ₂ MoO ₄ (2H ₂ O)	0.015
30	VOSO ₄ (2H ₂ O)	0.015
	CoCl ₂ (6H ₂ O)	0.005

C. Isothiazolone Structure

Isothiazolones included in the examples are designated as follows:

- 1) Isothiazolone A: 75% 5-chloro-2-methyl-3-isothiazolone plus 25% 2-methyl-3-isothiazolone
- 2) Isothiazolone B: 4,5-dichloro-2-n-octyl-3-isothiazolone
- 3) Isothiazolone C: 2-n-octyl-3-isothiazolone

EXAMPLE 1

Using a pure culture of *Chlorella pyrenoidosa* (green algae), various combinations of oxyfluorfen (acetone solution) and Isothiazolone A were subjected to MIC determinations (Bristol's Medium).

	MIC alone (ppm)	MIC combination (ppm)
<u>Compound</u>		
Oxyfluorfen	0.125	0.016
		SI = 0.63
Isothiazolone A	0.50	0.25

EXAMPLE 2

In a manner similar to EXAMPLE 1, another MIC study was conducted with oxyfluorfen (acetone solution) and Isothiazolone A. Concentrations for oxyfluorfen ranged from 0.0019 to 2.0 ppm and for Isothiazolone A, from 0.0078 to 0.5 ppm (Modified Allen's Medium).

	MIC alone (ppm)	MIC combination (ppm)
<u>Compound</u>		
Oxyfluorfen	1.0	0.125
		SI = 0.62
Isothiazolone A	0.25	0.125

EXAMPLE 3

In a manner similar to EXAMPLE 1, a pure culture of *Anabaena flos-aquae* (cyanobacteria) was used with various combinations of oxyfluorfen (acetone solution) and Isothiazolone B (Bristol's Medium).

	MIC alone (ppm)	MIC combination (ppm)
<u>Compound</u>		
Oxyfluorfen	>0.50*	0.064
		SI = <0.61
Isothiazolone B	1.25	0.60

* exceeded the range tested in this experiment

EXAMPLE 4

In a manner similar to EXAMPLE 1, a pure culture of *Chlorella pyrenoidosa* was used with various combinations of oxyfluorfen (emulsifiable concentrate) and Isothiazolone B. Concentrations of oxyfluorfen ranged from 0.0019 to 2.0 ppm and for Isothiazolone B, from 0.0078 to 0.5 ppm (Modified Allen's Medium).

<u>Compound</u>	MIC alone (ppm)	MIC combination (ppm)
Oxyfluorfen	2.0	1.0
		SI = 0.63
Isothiazolone B	0.06	0.008
Oxyfluorfen	2.0	0.25
		SI = 0.62
Isothiazolone B	0.06	0.03

EXAMPLE 5

In a manner similar to EXAMPLE 1, a pure culture of *Chlorella pyrenoidosa* was used with various combinations of oxyfluorfen (acetone solution) and Isothiazolone C. Concentrations for oxyfluorfen ranged from 0.0078 to 0.5 ppm and for Isothiazolone C, from 0.00049 to 0.5 ppm (Modified Allen's Medium).

<u>Compound</u>	MIC alone (ppm)	MIC combination (ppm)
Oxyfluorfen	0.5	0.25
		SI = 0.62
Isothiazolone C	0.5	0.06
Oxyfluorfen	0.5	0.125
		SI = 0.75
Isothiazolone C	0.5	0.25

EXAMPLE 6

In a manner similar to EXAMPLE 5, a pure culture of *Chlorella pyrenoidosa* was used with various combinations of oxyfluorfen (emulsifiable concentrate) and Isothiazolone C. Concentrations for oxyfluorfen ranged

from 0.00098 to 1.0 ppm and for Isothiazolone C, from 0.16 to 10.0 ppm (Modified Allen's Medium).

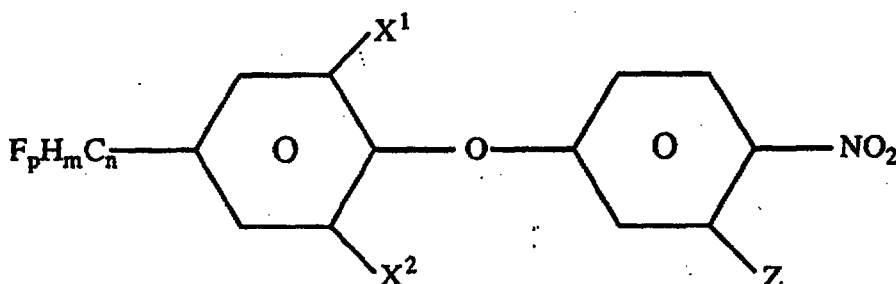
<u>Compound</u>	MIC alone (ppm)	MIC combination (ppm)
Oxyfluorfen	>1.0*	0.25
Isothiazolone C	1.25	0.63

SI = <0.75

* Exceeded the range tested in this experiment

Claims

1. Anti-algal composition comprising
(A) a compound of the formula



wherein

X¹, X²

Z

are each independently hydrogen, halogen, trihalomethyl, cyano, or (C₁ to C₄) alkyl;
is hydrogen, halogen, cyano, carboxy or salt thereof, lower alkylthio, lower carbalkoxy, lower carboxyalkyl, lower carbalkoxyalkyl, lower carbalkoxyalkoxycarbonyl, lower carbalkoxyalkoxy, lower alkoxy, lower cycloalkoxy, lower alkenyl, lower alkyl, lower cycloalkyl, unsubstituted or substituted amino, or R²O in which R² represents a hydrogen atom or the ester bonded acid radical of an inorganic or organic oxyacid;

p

m

where

n is an integer of 1 to 5 and m+p = 2n+1; and
(B) a 3-isothiazolone.

2. Composition according to claim 1 wherein the substituent Z of said compound (A) is not unsubstituted or substituted amino, nor R²O in which R² represents a hydrogen atom or the ester bonded acid radical of an inorganic or organic oxyacid.
3. Composition according to claim 2 wherein said compound (A) is of the formula



from 0.00098 to 1.0 ppm and for Isothiazolone C, from 0.16 to 10.0 ppm (Modified Allen's Medium).

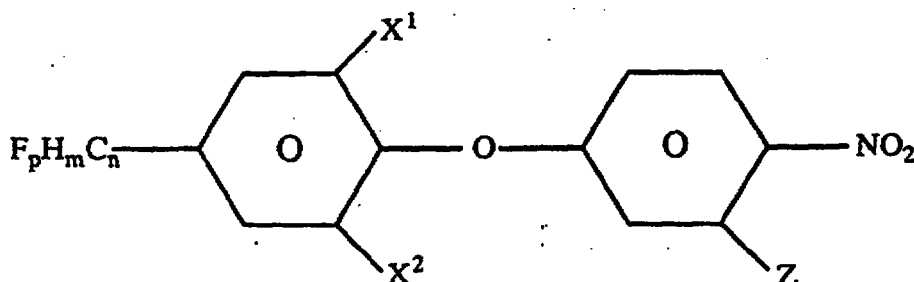
<u>Compound</u>	MIC alone (ppm)	MIC combination (ppm)
Oxyfluorfen	>1.0*	0.25
Isothiazolone C	1.25	0.63

SI = <0.75

* Exceeded the range tested in this experiment

Claims

1. Anti-algal composition comprising
(A) a compound of the formula



wherein

X¹, X²

Z

are each independently hydrogen, halogen, trihalomethyl, cyano, or (C₁ to C₄) alkyl;

is hydrogen, halogen, cyano, carboxy or salt thereof, lower alkylthio, lower carbalkoxy, lower carboxyalkyl, lower carbalkoxyalkyl, lower carbalkoxyalkoxycarbonyl, lower carbalkoxyalkoxy, lower alkoxy, lower cycloalkoxy, lower alkenyl, lower alkyl, lower cycloalkyl, unsubstituted or substituted amino, or R²O in which R² represents a hydrogen atom or the ester bonded acid radical of an inorganic or organic oxyacid;

p is an integer from 1 to 2n+1;

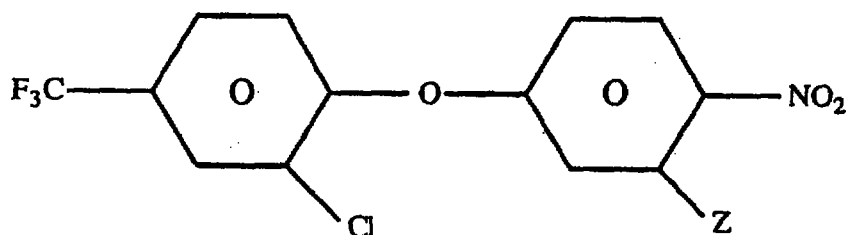
m is an integer of 0 to 2n;

where

n is an integer of 1 to 5 and m+p = 2n+1; and

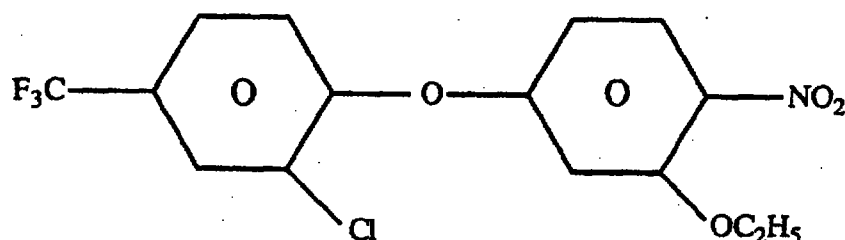
(B) a 3-isothiazolone.

2. Composition according to claim 1 wherein the substituent Z of said compound (A) is not unsubstituted or substituted amino, nor R²O in which R² represents a hydrogen atom or the ester bonded acid radical of an inorganic or organic oxyacid.
3. Composition according to claim 2 wherein said compound (A) is of the formula

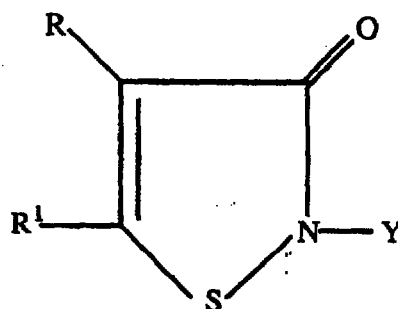


10 wherein Z is alkoxy, carboxy or salt thereof, carbalkoxyalkoxy, or $-\text{CO}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$.

4. Composition according to claim 3 wherein said compound (A) is oxyfluorfen of the formula



- 25 5. Composition according to any preceding claim wherein said 3-isothiazolone is of the formula



wherein

40 Y is: $(\text{C}_1-\text{C}_{18})$ alkyl or $(\text{C}_3-\text{C}_{12})$ cycloalkyl each optionally substituted with one or more of hydroxy, halo, cyano, alkylamino, dialkylamine, arylamino, carboxy, carbalkoxy, alkoxy, aryloxy, alkylthio, arylthio, haloalkoxy, cycloalkylamino, carbamoyl, or isothiazolonyl; an unsubstituted or halo-substituted (C_2-C_8) alkenyl or alkynyl; a $(\text{C}_7-\text{C}_{10})$ aralkyl optionally substituted with one or more of halogen, (C_1-C_4) alkyl or (C_1-C_4) alkoxy; or an aryl optionally substituted with one or more of halogen, nitro, (C_1-C_4) alkyl, (C_1-C_4) alkyl-acylamino, carb (C_1-C_4) alkoxy or sulfamyl;

45 R is hydrogen, halo, or a (C_1-C_4) alkyl; and

R¹ is hydrogen, halo or (C_1-C_4) alkyl.

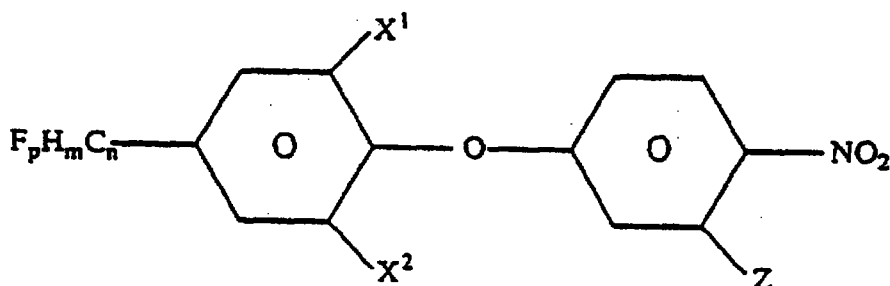
- 50 6. Composition according to claim 5 wherein Y is methyl, ethyl, propyl, isopropyl, butyl, hexyl, octyl, cyclohexyl, benzyl, 3,4-dichlorobenzyl, 4-methoxybenzyl, 3,4-dichlorophenyl, 4-methoxyphenyl, 4-chlorophenyl, 4-chlorobenzyl, hydroxymethyl, chloromethyl, phenethyl, 2-(4-chlorophenyl)ethyl, chloropropyl, or hydrogen.
- 55 7. Composition according to claim 5 wherein Y is $(\text{C}_1-\text{C}_{18})$ alkyl, $(\text{C}_3-\text{C}_{12})$ cycloalkyl, $(\text{C}_7-\text{C}_{10})$ aralkyl, or $(\text{C}_7-\text{C}_{10})$ ring-chlorinated aralkyl; R is hydrogen, methyl or chloro; and R¹ is hydrogen or chloro.
8. Composition according to any one of claims 1 to 4 wherein the isothiazolone is 4,5-dichloro-2-octyl-3-isothiazolone, 2-octyl-3-isothiazolone, 5-chloro-2-methyl-3-isothiazolone, or 2-methyl-3-isothiazolone.



9. Composition according to any preceding claim wherein the weight ratio of (A) to (B) is from about 0.1 to 100 to about 100 to 0.1.
10. Method of inhibiting or preventing the growth of algae in a locus subject or susceptible to contamination thereby, comprising incorporating into or onto the locus a composition according to any preceding claim in an amount effective to adversely affect the growth of said algae.
11. Method according to Claim 10, wherein the locus is cooling tower water and the algicidal composition is maintained at a concentration of from about 0.005 to about 20 ppm, preferably 0.1 to 10 ppm, more preferably 0.2 to 2 ppm, in the water.
12. Method according to claim 10, wherein the locus is a coating or impregnant composition, and the algicidal composition is incorporated in an amount of from about 0.1 ppm to about 2 percent, preferably about 1 ppm to 1 percent, more preferably about 10 ppm to 4000 ppm.
13. Method according to claim 9, wherein the locus is an aquarium, fish hatchery, shrimp pond, finfish pond, mollusc cultivator, crustacean cultivator, swimming pool, lake, fountain, settling pond, separation pond, waste treatment pond, spray pond, water treatment pond, hydroponic farming site, or pulp or paper manufacturing water.
14. Coating or impregnant composition comprising from about 0.1 ppm to about 2 percent, preferably from about 10 to about 4000 ppm, of the composition of any one of claims 1 to 9.
15. Marine antifoulant composition comprising about 1 to 10 percent of the composition of any one of claims 1 to 9.
16. Stucco, roof mastic, wall mastic, masonry coating or plastic composition comprising an effective amount of the composition of any one of claims 1 to 9.

Patentansprüche

1. Algizide Zusammensetzung enthaltend
(A) eine Verbindung der Formel



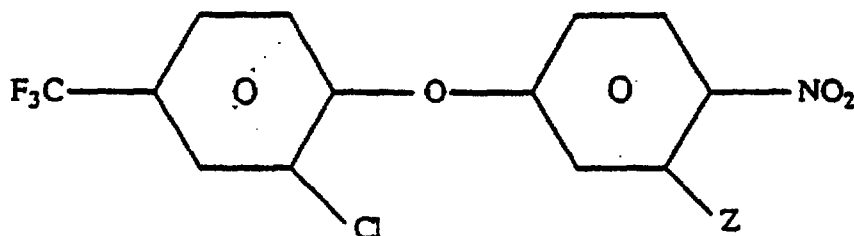
in der X^1 , X^2 jeweils unabhängig Wasserstoff, Halogen, Trihalomethyl, Cyano oder (C_1-C_4) -Alkyl sind, Z ist Wasserstoff, Halogen, Cyano, Carboxy oder Salz desselben, niederes Alkylthio, niederes Carbalkoxy, niederes Carboxyalkyl, niederes Carbalkoxyalkyl, niederes Carbalkoxyalkoxycarbonyl, niederes Carbalkoxyalkoxy, niederes Alkoxy, niederes Cycloalkoxy, niederes Alkenyl, niederes Alkyl, niederes Cycloalkyl, unsubstituiertes oder substituiertes Amino oder R^2O , in der R^2 ein Wasserstoffatom oder die Esterbindung mit einem Säurerest einer anorganischen oder organischen Oxsäure ist, p ist eine ganze Zahl von 1 bis $2n+1$, m ist eine ganze Zahl von 0 bis $2n$, wobei n eine ganze Zahl von 1 bis 5 ist und $m+p=2n+1$ und (B) ein 3-Isothiazolon.

2. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß der Substituent Z in Verbindung (A) weder nicht substituiertes Amino oder substituiertes Amino, noch



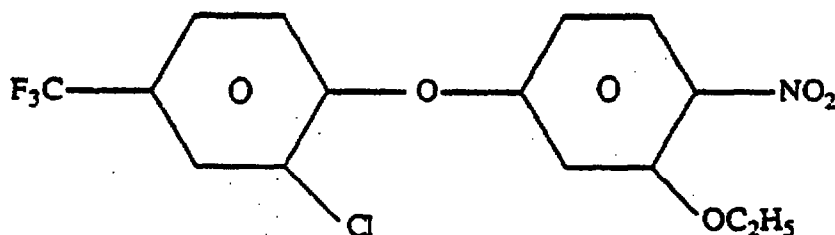
R^2O ist, wobei R^2 ein Wasserstoffatom oder eine Esterbindung eines Säurerestes einer anorganischen oder organischen Oxsäure ist.

3. Zusammensetzung nach Anspruch 2, dadurch gekennzeichnet, daß die Verbindung (A) die Formel aufweist



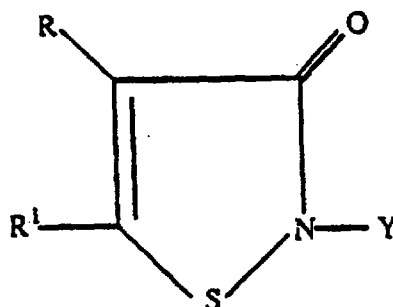
in der Z Alkoxy, Carboxy oder Salz desselben, Carbalkoxyalkoxy oder $-CO_2CH_2CO_2C_2H_5$ ist.

4. Zusammensetzung nach Anspruch 3, dadurch gekennzeichnet, daß die Verbindung (A) Oxyfluorfen der Formel



ist.

5. Zusammensetzung nach einem der vorstehenden Ansprüche 1-4, dadurch gekennzeichnet, daß das 3-Isotiazolon die Formel aufweist



in der Y (C_1-C_{18}) -Alkyl oder (C_3-C_{12}) -Cycloalkyl ist, jeweils gegebenenfalls substituiert mit einem oder mehreren von Hydroxy, Halogen, Cyano, Alkylamino, Dialkylamin, Arylamino, Carboxy, Carbalkoxy, Alkoxy, Aryloxy, Alkylthio, Arylthio, Haloalkoxy, Cycloalkylamino, Carbamoxycy oder Isothiazolonyl, ein unsubstituiertes oder mit Halogen substituiertes (C_2-C_8) -Alkenyl oder Alkynyl, ein (C_7-C_{10}) -Aralkyl, gegebenenfalls substituiert mit einem oder mehreren von Halogen, (C_1-C_4) -Alkyl oder (C_1-C_4) -Alkoxy, oder ein Aryl, gegebenenfalls substituiert mit einem oder mehreren von Halogen, Nitro, (C_1-C_4) -Alkyl, (C_1-C_4) -Alkyl-Acylamino, Carb (C_1-C_4) -Alkoxy oder Sulfamyl,



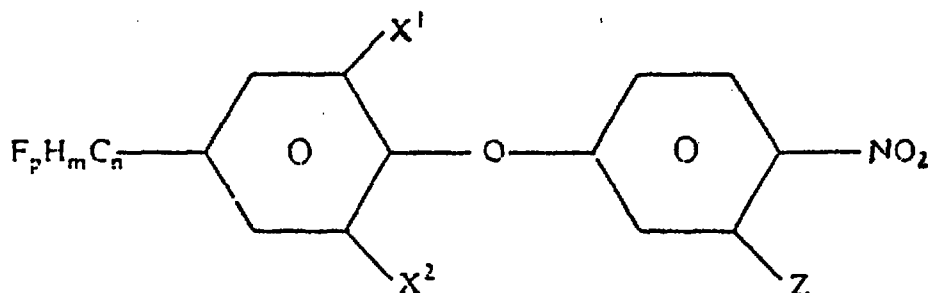
R Wasserstoff, Halogen oder eine (C₁-C₄)-Alkylgruppe ist und
R¹ Wasserstoff, Halogen oder eine (C₁-C₄)-Alkylgruppe ist.

6. Zusammensetzung nach Anspruch 5,
dadurch gekennzeichnet,
daß Y Methyl, Ethyl, Propyl, Isopropyl, Butyl, Hexyl, Octyl, Cyclohexyl, Benzyl, 3,4-Dichlorbenzyl, 4-Methoxybenzyl, 3,4-Dichlorphenyl, 4-Methoxyphenyl, 4-Chlorphenyl, 4-Chlorbenzyl, Hydroxymethyl, Chlormethyl, Phenethyl, 2-(4-Chlorphenyl)ethyl, Chloropropyl oder Wasserstoff ist.
7. Zusammensetzung nach Anspruch 5,
dadurch gekennzeichnet,
daß Y (C₁-C₁₈)-Alkyl, (C₃-C₁₂)-Cycloalkyl, (C₇-C₁₀)-Aralkyl oder (C₇-C₁₀)-ringchloriertes Aralkyl ist, R Wasserstoff, Methyl oder Chlor ist und R¹ Wasserstoff oder Chlor ist.
8. Zusammensetzung nach einem der Ansprüche 1-4,
dadurch gekennzeichnet,
daß das Isothiazolon 4,5-Dichlor-2-octyl-3-isothiazolon, 2-Octyl-3-isothiazolon, 5-Chlor-2-methyl-3-isothiazolon oder 2-Methyl-3-isothiazolon ist.
9. Zusammensetzung nach einem der Ansprüche 1-8,
dadurch gekennzeichnet,
daß das Gewichtsverhältnis von (A):(B) von etwa 0,1-100: etwa 100-0,1 beträgt.
10. Verfahren zum Hemmen oder Verhindern des Wachstums von Algen an einem Ort, der gegenüber Verunreinigung durch Algen empfindlich ist, durch Einbringen in oder auf die Stelle einer Zusammensetzung nach einem der vorstehenden Ansprüche in einer wirksamen Menge, um das Wachstum der Algen gegenteilig zu beeinflussen.
11. Verfahren nach Anspruch 10,
dadurch gekennzeichnet,
daß die Stelle Wasser in einem Kühlwasserturm ist und die algizide Zusammensetzung im Wasser in einer Konzentration aufrechterhalten wird von etwa 0,005 bis etwa 20 ppm, vorzugsweise 0,1 bis 10 ppm, ganz besonders bevorzugt 0,2 bis 2 ppm.
12. Verfahren nach Anspruch 10,
dadurch gekennzeichnet,
daß die Stelle eine Beschichtungszusammensetzung oder Imprägnierzusammensetzung ist und die algizide Zusammensetzung in einer Menge von etwa 0,1 ppm bis etwa 2%, vorzugsweise etwa 1 ppm bis 1%, ganz besonders bevorzugt etwa 10 ppm bis 4000 ppm zugesetzt wird.
13. Verfahren nach Anspruch 9,
dadurch gekennzeichnet,
daß die Stelle ein Aquarium, Fischbrutbecken, Garnelenteich, Flnnfischteich, Muschelzuchtanlage, Krustentierzuchtanlage, Schwimmbecken, See, Springbrunnen, Absetzbecken, Trennbecken, Abwasserbehandlungsbecken, Spritzbecken, Wasserbehandlungsbecken, Hydrokulturlpflanzzuchtanlage oder Celluloseherstellungs- oder Papierherstellungswasser ist.
14. Beschichtungs- oder Imprägnierzusammensetzung, enthaltend von etwa 0,1 ppm bis etwa 2%, vorzugsweise von etwa 10 bis etwa 4000 ppm der Zusammensetzung nach einem der Ansprüche 1 bis 9.
15. Unterwasser-Antifoulingzusammensetzung, enthaltend etwa 1 bis 10% der Zusammensetzung nach einem der Ansprüche 1 bis 9.
16. Gips-, Dachmastix-, Wandmastix-, Mauerbeschichtungs- oder Kunststoffzusammensetzung, enthaltend eine wirksame Menge der Zusammensetzung nach einem der Ansprüche 1 bis 9.



Revendications

1. Composition anti-algues comprenant :
(A) un composé de formule :



dans laquelle :

X^1, X^2 sont tous deux indépendamment de l'hydrogène, un halogène, un groupe trihalométhyle, cyano ou alkyle en (C_1-C_4) , et

Z est de l'hydrogène, un halogène, un groupe cyano, carboxy ou un de leurs sels, un groupe alkylthio inférieur, carbalkoxy inférieur, carboxyalkyle inférieur, carbalkoxyalkyle inférieur, carbalkoxyalkoxycarbonyle inférieur, carbalkoxyalkoxy inférieur, alkoxy inférieur, cycloalkoxy inférieur, alkényle inférieur, alkyle inférieur, cycloalkyle inférieur, amino non substitué ou substitué ou R^2O dans lequel R^2 représente un atome d'hydrogène ou le radical acide lié par ester d'un oxyacide minéral ou organique;

P est un nombre entier de 1 à $2n+1$;

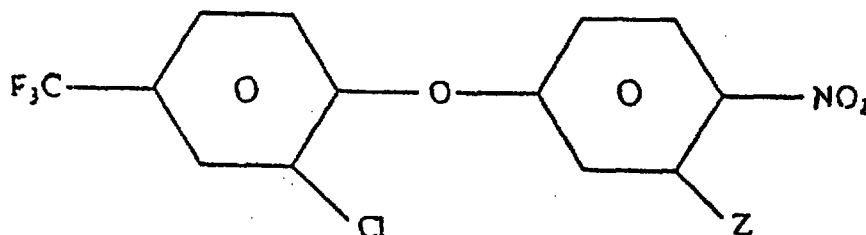
m est un nombre entier de 0 à $2n$;

où n est un nombre entier de 1 à 5 et $m+p = 2n+1$;

et (B) une 3-isothiazolone.

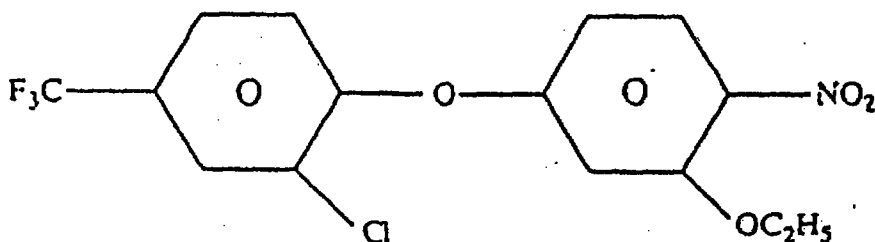
2. Composition selon la revendication 1, dans laquelle le substituant Z dudit composé (A) n'est pas un groupe amino non substitué ou substitué ni R^2O dans lequel R^2 représente un atome d'hydrogène ou le radical acide lié par ester d'un oxyacide minéral ou organique.

3. Composition selon la revendication 2, dans laquelle ledit composé (A) a pour formule :

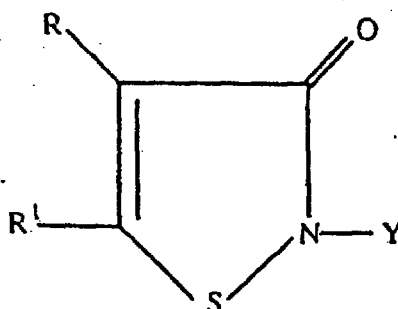


dans laquelle Z est un groupe alkoxy, carboxy ou un sel de ces groupes, un groupe carbalkoxyalkoxy ou $CO_2CH_2CO_2C_2H_5$.

4. Composition selon la revendication 3, dans laquelle ledit composé (A) est l'oxyfluorène qui a pour formule :



5. Composition selon l'une quelconque des revendications précédentes, dans laquelle ladite 3-isothiazolone a pour formule:



dans laquelle Y est un groupe alkyle en C₁-C₁₈ ou cycloalkyle en C₃-C₁₂, chacun d'entre eux étant éventuellement substitué par un ou plusieurs des groupes hydroxy, halogéno, cyano, alkylamino, dialkylamino, arylamino, carboxy, carbalkoxy, alkoxy, aryloxy, alkylthio, arylthio, haloalkoxy; cycloalkylamino, carbamoxo ou isothiazolonyl; un groupe alkényle ou alkynyle en C₂-C₈ non substitué ou substitué par un groupe halogène; un groupe aralkyle en C₇-C₁₀ facultativement substitué par un ou plusieurs des groupes halogène, alkyle en C₁-C₄ ou alkoxy en C₁-C₄; ou un groupe aryle facultativement substitué par un ou plusieurs des groupes halogène, nitro, alkyle en C₁-C₄, alkyl en C₁-C₄, acylamino, carbalkoxy en C₁-C₄ ou sulfamyle;

R est de l'hydrogène, un groupe halogéno ou un groupe alkyle en C₁-C₄; et

R' est de l'hydrogène, un groupe halogéno ou alkyle en C₁-C₄.

6. Composition selon la revendication 5, dans laquelle ledit groupe Y est un groupe méthyle, éthyle, propyle, isopropyle, butyle, hexyle, octyle, cyclohexyle, benzyle, 3,4-dichlorobenzyle, 4-méthoxybenzyle, 4-chlorobenzyle, hydroxyméthyle, 3,4-dichlorophényle, 4-méthoxyphényle, 4-chlorophényle, chlorométhyle, phénéthyle, 2-(4-chlorophényl)éthyle, chloropropyle ou de l'hydrogène.
7. Composition selon la revendication 5, dans laquelle Y est un groupe alkyle en C₁-C₁₈, un groupe cycloalkyle en C₃-C₁₂, un groupe aralkyle en C₇-C₁₀ ou un groupe aralkyle chloré dans le noyau en C₇-C₁₀; R est de l'hydrogène, un groupe méthyle ou chloro; et R' est de l'hydrogène ou un groupe chloro.
8. Composition selon l'une quelconque des revendications 1 à 4, dans laquelle l'isothiazolone est la 4,5-dichloro-2-octyl-3-isothiazolone, la 2-octyl-3-isothiazolone, la 5-chloro-2-méthyl-3-isothiazolone ou la 2-méthyl-3-isothiazolone.
9. Composition selon l'une quelconque des revendications précédentes, dans laquelle le rapport pondéral de (A) à (B) est d'environ 0,1:100 à environ 100:0,1.
10. Procédé d'inhibition ou de prévention de la croissance d'algues dans un lieu sujet à contamination où susceptible de se contaminer, ce procédé consistant à incorporer dans ou sur le lieu une composition selon l'une quelconque des revendications précédentes en quantité efficace pour affecter de manière désavantageuse la croissance desdites algues.
11. Procédé selon la revendication 10, dans lequel le lieu est une tour d'eau de refroidissement et la composition algicide est maintenue à une concentration d'environ 0,005 à environ 20 ppm, de préférence une



concentration d'environ 0,1 à 10 ppm et bien mieux encore une concentration d'environ 0,2 à 2 ppm par rapport à l'eau.

- 5 12. Procédé selon la revendication 10, dans laquelle le lieu est une composition de revêtement ou d'imprégnation et la composition algicide est incorporée selon une concentration d'environ 0,1 ppm à environ 2 %, de préférence selon une concentration d'environ 1 ppm à 1 %, mieux encore selon une concentration d'environ 10 à 4.000 ppm.
- 10 13. Procédé selon la revendication 9, dans laquelle le lieu est un aquarium, un alevinage, un étang à crevettes, un étang à poisson, un élevage de mollusques, un élevage de crustacés, une piscine, un lac, une fontaine, un bassin de décantation, un bassin de séparation, un bassin de traitement des eaux usées, un réservoir de pulvérisation, un bassin de traitement de l'eau, un site de culture hydroponique ou l'eau de fabrication de pâte ou de papier.
- 15 14. Composition de revêtement ou d'imprégnation comprenant environ 0,1 ppm à environ 2 %, de préférence environ 10 à environ 4.000 ppm de la composition de l'une quelconque des revendications 1 à 9.
- 15 15. Composition anti-salissure marine comprenant environ 1 à 10 % de la composition de l'une quelconque des revendications 1 à 9.
- 20 16. Stuc, mastic de toiture, mastic mural, revêtement de maçonnerie ou composition plastique comprenant une quantité efficace de la composition de l'une quelconque des revendications 1 à 9.
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