

Description

The present invention concerns to antialgal compositions, comprising combinations of diphenylethers and sodium hypochlorite.

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.

EP-A-384661 discloses the use of diphenylethers in antialgal compositions, and U.S.-A-4,975,111 discloses the use of said diphenylethers with isothiazolones as antialgal compositions.

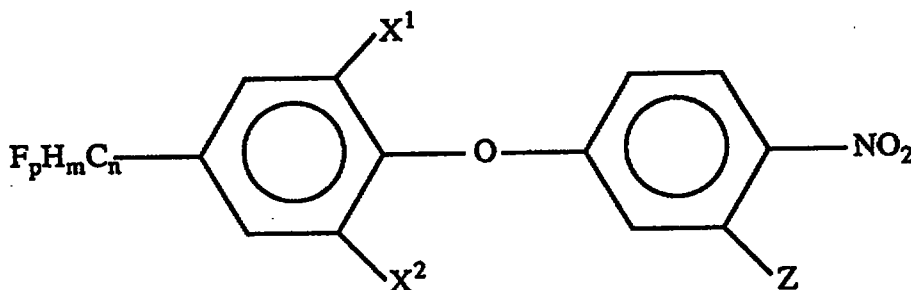
EP-A-143547 teaches the use of oxyfluorfen diphenylether/glyphosate (N-(phosphonomethyl)glycine) mixtures as having enhanced herbicidal activity towards weeds and grasses, but no antialgal activity is disclosed.

Oxyfluorfen in combination with diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) has been found to be an effective herbicide for weed control in sugarcane fields (HJ Yeh, *Taiwan Sugar*, 27(4), 125-129, 1980), nectarine crops (MJ Hartley, *Proc. N.Z. Weed Pest Control Conf.*, 40th, 140-143, 1987), and biomass production (P Felker and CE Russell, *J. Hortic. Sci.*, 63(1), 149-155, 1988).

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.

We have discovered that the antialgal activity of diphenyl ethers can be enhanced to an unexpectedly large degree by combination with sodium hypochlorite. Accordingly the present invention provides in a first aspect a composition comprising

(A) a diphenylether compound of the formula



wherein

- X¹, X² are each independently hydrogen, halogen, trihalomethyl, cyano, or (C₁-C₄)alkyl,
 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 lower alkyl amino, or RO in which R represents a hydrogen atom or an 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;
 n is an integer of 1 to 5;
 m+p = 2n+1

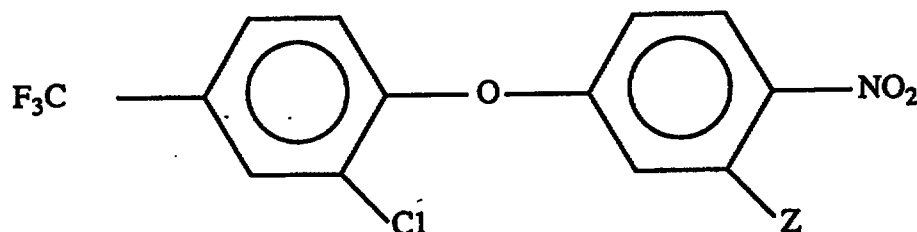
and (B) sodium hypochlorite, wherein the ratio of (A) to (B) is from 1/20 to 1/1 by weight.

In another aspect, the invention comprises a method for inhibiting the growth of algae in a locus subject to contamination by algae, which comprises incorporating onto or into the locus, a composition comprising the aforementioned diphenylethers and sodium hypochlorite in an amount which is effective to adversely affect the growth of algae.

The invention also includes within its scope algae-resistant coating or impregnant compositions and marine anti-foulant compositions containing the antialgal composition.

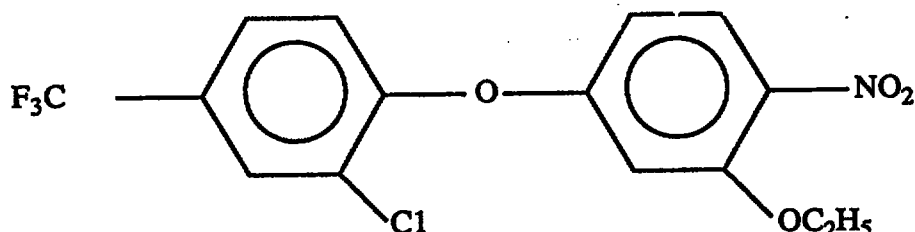
Where the expression "lower" is employed in conjunction with terms, such as alkyl, alkoxy, etc., it is intended to indicate that the alkyl or alkyl portion thereof has 1 to 6 carbon atoms, i.e., (C₁-C₆).

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



wherein Z is selected from the group consisting of alkoxy, carboxy or salt thereof, carbalkoxyalkoxy, and -CO₂CH₂CO₂C₂H₅.

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



An especially useful aspect of the invention is in controlling algae in cooling tower water, and in a preferred embodiment, it is maintaining a concentration of about 0.005 to about 20 ppm of the anti-algal composition in the cooling tower water, 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 comprising incorporation of the composition of the invention in the coating or impregnant, preferably at a concentration 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.

Algae-resistant coating or impregnant compositions provided by the invention preferably comprise about 0.1 ppm to about 2 percent of the antialgal composition, more preferably about 10 to 4000 ppm.

In a marine-antifoulant composition, on the other hand, the antialgal composition of the invention comprises about 1 to 15 percent of the antifoulant composition.

In the protection of fabric, leather, paper or wood materials, the microbicidal composition is added at a concentration of from about 0.1 ppm to about 2 percent by weight. In aqueous media, the microbicidal composition comprises from about 0.1 ppm to about 1 percent of the aqueous system depending on the specific end use; for example, in cooling water tower applications, in the protection of solid surfaces by the application of algicidal washes and with pulp or paper manufacturing processes, the microbicidal composition is added at a concentration from about 0.01 to about 20 ppm by weight.

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, spray ponds, water 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.

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 without departing from scope of the invention.

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. Eisman, 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, which inhibits growth

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

Q_b = quantity of compound B, in mixture, which inhibits growth

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/commercial biocide 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) and are listed in Table 1. Mixed cooling tower cultures were obtained from surface scrapings of industrial cooling towers. 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 well 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).

Table 1

Pure Cultures of Green Algae and Cyanobacteria Used in MIC and Combination Studies	
Organisms	UTEX ID #
Green Algae (Chlorophyceae)	
<i>Chlorella pyrenoidosa</i>	1230
<i>Scenedesmus quadricauda</i>	614
Blue-Green Bacteria (Cyanobacteria)	
<i>Anabaena flos-aquae</i>	1444
<i>Nostoc commune</i>	584

B. Preparation of Modified Allen's Media Formulation (pH 6.3)

Component	Concentration (mg/l)
NaNO ₃	250
CaCl ₂ (2H ₂ O)	31
MgSO ₄ (7H ₂ O)	75
NaCl	25
KH ₂ PO ₄	175
K ₂ HPO ₄	75
FeCl ₃ (6H ₂ O)	7.5
Na ₂ (EDTA)	10.3
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
CuCl ₂ (2H ₂ O)	0.025
Na ₂ MoO ₄ (2H ₂ O)	0.015
VO ₂ SO ₄ (2H ₂ O)	0.015
CoCl ₂ (6H ₂ O)	0.005

Descriptions of oxyfluorfen sodium hypochlorite are provided below:
oxyfluorfen: 98% technical grade
sodium hypochlorite: aqueous bleach, 5.25% active ingredient

EXAMPLE 1

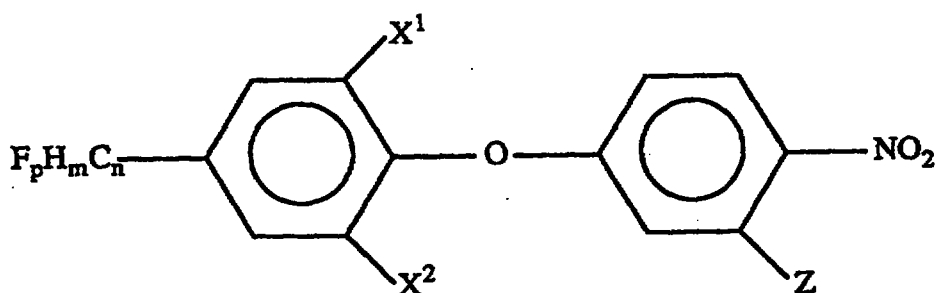
Using a pure culture of *Chlorella pyrenoidosa* (green alga), various combinations of oxyfluorfen (acetone solution) and Compound B (in water) were subjected to MIC determinations in modified Allen's medium. In this example, Compound (A) is oxyfluorfen and Compound (B) is sodium hypochlorite. Concentrations (Q_a , Q_b) are expressed in ppm in this example and all the following examples.

Q_a	Q_b	Q_a/Q_b	SI
0	$2.0 (Q_B)$		-1.0
0.094	1.0	1/11	0.56
0.187	1.0	1/5	0.62
0.375	1.0	1/3	0.75
$1.5 (Q_A)$	0	--	1.0

Claims

1. Composition comprising

(A) a diphenylether compound of the formula

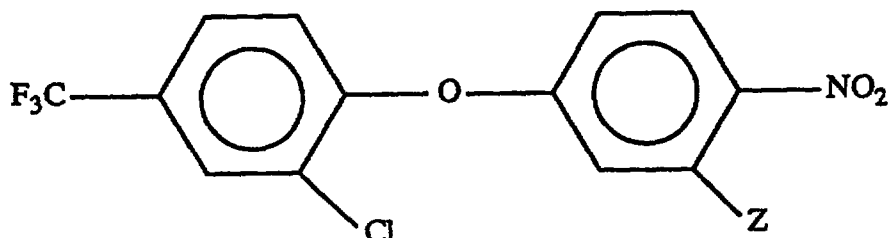


wherein

- X^1, X^2 are each independently hydrogen, halogen, trihalomethyl, cyano, and (C_1-C_4) alkyl;
 Z is hydrogen, halogen, cyano, carboxy or salt thereof, lower alkylthio, lower carbalkoxy, lower carboxy-alkyl, lower carbalkoxyalkyl, lower carbalkoxyalkoxycarbonyl, lower carbalkoxyalkoxy, lower alkoxy, lower cycloalkoxy, lower alkenyl, lower alkyl, lower cycloalkyl, unsubstituted or lower alkyl amino, RO in which R represents a hydrogen atom or an 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 $2n$;
 n is an integer of 1 to 5;
 $m+p = 2n+1$

and (B) sodium hypochlorite, wherein the ratio of (A) to (B) is from 1/20 to 1/1 by weight.

2. Composition according to claim 1 wherein (A) is of the formula



in which Z is lower alkoxy, lower carboxy or salt thereof, lower carbalkoxyalkoxy, and $-CO_2CH_2CO_2C_2H_5$, preferably OC_2H_5 .

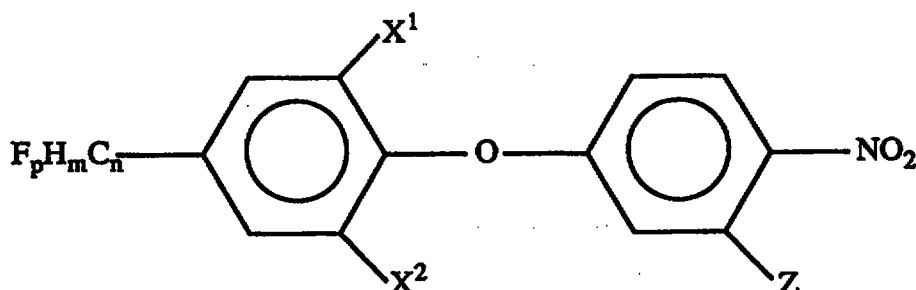


Q_a	Q_b	Q_a/Q_b	SI
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0.094	1.0	1/11	0.56
0.187	1.0	1/5	0.62
0.375	1.0	1/3	0.75
1.5 (Q_A)	0	--	1.0

Claims

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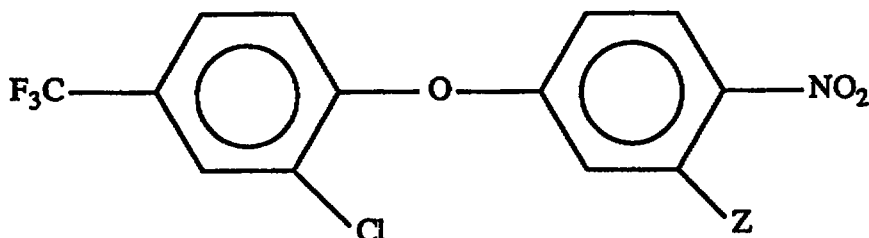


wherein

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 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 lower alkyl amino, RO in which R represents a hydrogen atom or an ester bonded acid radical of an inorganic or organic oxyacid;
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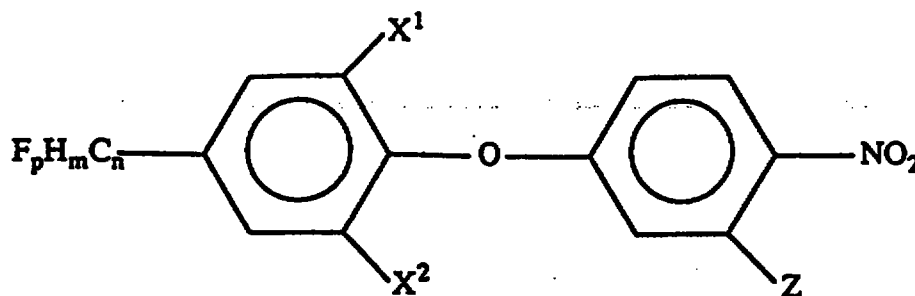


3. A coating or impregnant composition comprising from 0.1 ppm to 2 percent by weight of a composition according to claims 1 or 2.
4. A marine antifoulant composition, an algae-resistant stucco, roof mastic, wall mastic, or masonry coating, or an algae-resistant plastic composition each comprising from 1 to 15 ppm of a composition according to claims 1 or 2.
5. Method of preventing or inhibiting the growth of algae in a locus susceptible or subject to contamination thereby, which comprises incorporating onto or into the locus, in an amount effective to adversely affect said growth, a composition according to any preceding claim.
6. Method according to claim 5 wherein the locus is an aqueous medium and said composition is used in an amount from 0.1 ppm to 1 percent by weight, or a coating or impregnant composition and said composition is used in an amount from 0.1 ppm to 2 percent by weight, or a marine antifoulant composition and said composition is used in an amount from 1 to 10 percent by weight, or a pulp or paper manufacturing process and said composition is used in an amount from 0.1 to 1000 ppm by weight, or cooling tower water and said composition is used in an amount from 0.005 to 20 ppm by weight, or fabric, leather, paper or wood and said composition is used in an amount from 0.1 ppm to 2 percent by weight.
7. The use of a composition as defined in any of claims 1 to 4 to inhibit or prevent the growth of algae.

Patentansprüche

1. Zusammensetzung enthaltend

(A) eine Diphenyletherverbindung der Formel



in der X¹, X² jeweils unabhängig Wasserstoff, Halogen, Trihalomethyl, Cyano und (C₁-C₄)-Alkyl sind, Z ist Wasserstoff, Halogen, Cyano, Carboxyl 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, nichtsubstituiertes oder niederes Alkylamino, RO, in dem R ein Wasserstoffatom oder ein als Ester gebundener Säurerest einer anorganischen oder organischen Oxosäure ist,

p ist eine ganze Zahl von 1 bis 2n+1,

m ist eine ganze Zahl von 0 bis 2n,

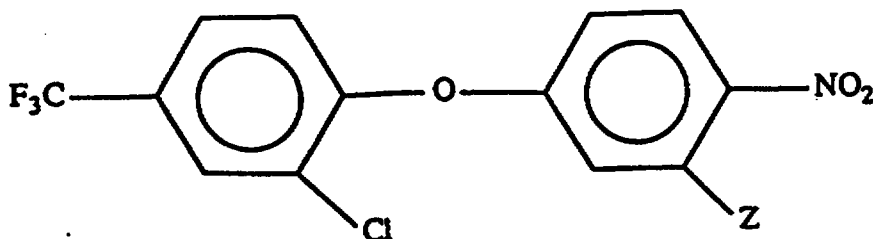
n ist eine ganze Zahl von 1 bis 5,

m+p=2n+1, und

(B) Natriumhypochlorit,

wobei das Gewichtsverhältnis von (A):(B) von 1:20 bis 1:1 beträgt.

2. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß (A) der Formel genügt



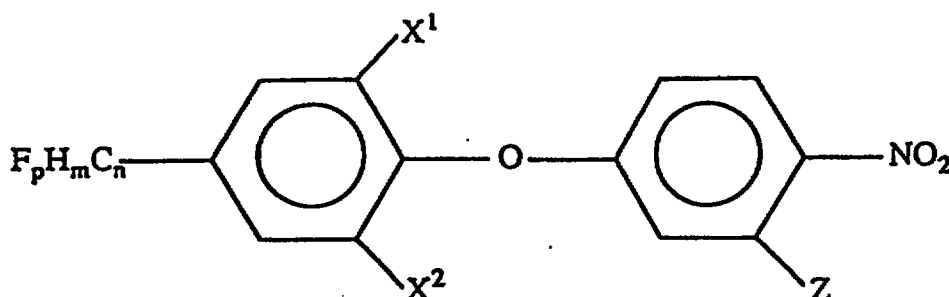
in der Z niederes Alkoxy, niederes Carboxy oder Salz desselben, niederes Carbalkoxyalkoxy und $-\text{CO}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$, vorzugsweise OC_2H_5 , ist.

3. Beschichtungs- oder Imprägnierzusammensetzung enthaltend von 0,1 ppm bis 2 %, bezogen auf Gewicht, einer Zusammensetzung nach Ansprüchen 1 oder 2.
4. Anwuchsverhindernde Unterwasseranstrichfarbe, algenbeständiger Außenputz, Dachasphalt, Wandmastix oder Mauerwerksbeschichtung oder algenbeständige Kunststoffzusammensetzung, jeweils enthaltend von 1-15 ppm einer Zusammensetzung nach Ansprüchen 1 oder 2.
5. Verfahren zum Verhindern oder Hemmen des Wachstums von Algen an einem Ort, der anfällig dafür oder damit befallen ist, durch Einbringen in oder auf den Ort einer das Wachstum wirksam gegenteilig beeinflussenden Menge einer Zusammensetzung nach einem der vorstehenden Ansprüche.
6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß der Ort ein wäßriges Medium ist und die Zusammensetzung in einer Menge von 0,1 ppm bis 1 %, bezogen auf Gewicht, verwendet wird oder eine Beschichtungs- oder Imprägnierzusammensetzung und die Zusammensetzung in einer Menge von 0,1 ppm bis 2 %, bezogen auf Gewicht, verwendet wird oder eine anwuchsverhindernde Unterwasseranstrichfarbe und die Zusammensetzung in einer Menge von 1 bis 10 Gew.-% verwendet wird oder ein Zellstoff- oder Papierherstellungsverfahren und die Zusammensetzung in einer Menge von 0,1 bis 1000 ppm, bezogen auf Gewicht, verwendet wird oder Wasser eines Kühlturmes und die Zusammensetzung in einer Menge von 0,005 bis 20 ppm, bezogen auf Gewicht, verwendet wird oder ein Gewebe, Leder, Papier oder Holz und die Zusammensetzung in einer Menge von 0,1 ppm bis 2 %, bezogen auf Gewicht, verwendet wird.
7. Verwendung einer Zusammensetzung nach einem der Ansprüche 1-4 zum Hemmen oder Verhindern des Wachstums von Algen.

Revendications

1. Composition comprenant

(A) un composé éther diphenylique de formule



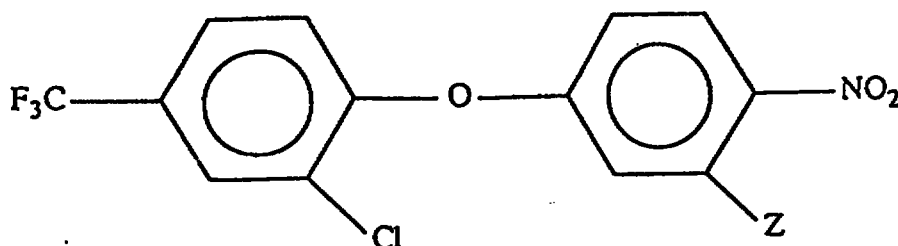
dans laquelle



- X¹, X²** sont chacun, indépendamment, un atome d'hydrogène, un atome d'halogène, et un groupe trihalogé-nométhyle, cyano et alkyle (en C₁-C₄);
- Z** est un atome d'hydrogène, un atome d'halogène, ou un groupe cyano, carboxy ou un de ses sels, alkylthio inférieur, carbalcoxy inférieur, carboxyalkyle inférieur, carbalcoxyalkyle inférieur, carbal-coxyalcoxy-carbonyle inférieur, carbalcoxyalcoxy inférieur, alcoxy inférieur, cycloalcoxy inférieur, alcényle inférieur, alkyle inférieur, cycloalkyle inférieur, alkylamino non substitué ou inférieur, RO, où R représente un atome d'hydrogène ou un radical acide, lié à un ester, d'un oxacide inorganique ou organique;
- p** est un nombre entier de 1 à 2n+1;
- m** est un nombre entier de 0 à 2n;
- n** est un nombre entier de 1 à 5;
- m+p = 2n+1 ; et

(B) l'hypochlorite de sodium, le rapport de (A) à (B) étant de 1/20 à 1/1 en poids.

2. Composition selon la revendication 1, dans laquelle (A) a pour formule



dans laquelle Z est un groupe alcoxy inférieur, carboxy inférieur ou un de ses sels, carbalcoxyalcoxy inférieur et -CO₂CH₂CO₂C₂H₅, de préférence OC₂H₅.

3. Composition de revêtement ou d'imprégnation, comprenant de 0,1 ppm à 2% en poids d'une composition selon la revendication 1 ou 2.
4. Composition marine antisalissure, stuc résistant aux algues, mastic de toiture, mastic de cloison ou revêtement de maçonnerie, ou composition plastique résistante aux algues, comprenant chacun de 1 à 15 ppm d'une composition selon la revendication 1 ou 2.
5. Procédé pour empêcher ou inhiber la croissance d'algues dans un lieu susceptible ou sujet à une contamination par les algues, qui comprend l'incorporation sur ou dans le lieu, en une quantité efficace pour affecter négativement ladite croissance, d'une composition selon l'une quelconque des revendications précédentes.
6. Procédé selon la revendication 5, dans lequel le lieu est un milieu aqueux et ladite composition est utilisée à raison de 0,1 ppm à 1% en poids, ou est une composition de revêtement ou d'imprégnation et ladite composition est utilisée à raison de 0,1 ppm à 2% en poids, ou est une composition marine antisalissure et ladite composition est utilisée à raison de 1 à 10% en poids, ou est un procédé de fabrication de pâte ou de papier et ladite composition est utilisée à raison de 0,1 à 1 000 ppm en poids, ou est une eau de tour de refroidissement et ladite composition est utilisée à raison de 0,005 à 20 ppm en poids, ou est du tissu, du cuir, du papier ou du bois et ladite composition est utilisée à raison de 0,1 ppm à 2% en poids.
7. Utilisation d'une composition telle que définie dans l'une quelconque des revendications 1 à 4 pour inhiber ou empêcher la croissance d'algues.