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**(54) Title:** METHODS FOR CONTROL AND MITIGATION OF MOLLUSCS

**(57) Abstract**

A method is provided for controlling the proliferation of molluscs in target habitat by applying to the habitat a compound or mixture of compounds which are amines, ethoxylated amines, quaternary amines, ethoxylated quaternary amines and cyclic amines.

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## METHODS FOR CONTROL AND MITIGATION OF MOLLUSCS

BACKGROUND OF THE INVENTION

The present invention is directed to methods of control and mitigation of molluscs and in particular, 5 the control of molluscs for macrofouling control within industrial cooling water systems and within municipal water supply systems. The bi-valve molluscs Dreissena polymorpha (Zebra mussel) and Corbicula fluminea (Asian clam) are macrofouling 10 species capable of settling in the service water systems (SWS) of electric power stations, water treatment stations, and other industrial systems which use fresh water from lakes and streams for heat exchange purposes. These molluscs can grow in sizes 15 to reduce or block flow in small diameter piping or heat exchangers. For C. fluminea, the problem primarily stems from the small juvenile molluscs which become suspended in intake waters and settle in low flow areas (such as the bottom of large diameter 20 piping, pipe bends, reservoirs, etc.). Once settled in these flow areas, the juveniles grow rapidly to sizes that will block the small diameter tubings. After growing to sizes capable of fouling the system components, the C. fluminea may crawl or be carried 25 by water currents from the low flow areas into high flow piping where they are transported to other areas

where their shells become lodged as constrictions in the tubing, thereby restricting or blocking flow.

The mode of action of D. polymorpha is somewhat different. The small larvae are carried into the 5 intake on water currents and settle in the low flow areas very similar to those described for C. fluminea. However, unlike C. fluminea which burrow into the sediment accumulated in the low flow areas, D. polymorpha adults produce proteinaceous byssal 10 threads from a byssal gland at the base of their foot to attach to hard surfaces. Since the juvenile D. polymorpha preferentially settle on open, hard surfaces, but also attach on the shells of attached adults, mats of mussels many shells thick develop in 15 low flow areas. Moreover, dead mussel shells and mats of mussel shells may break loose from the walls of the low flow areas and are carried into macrofouling sensitive components such as heat exchangers. Since the adults attach by byssal threads to hard surfaces 20 (including boat hulls) and the larvae remain for extended periods in the plankton, D. polymorpha have extensive capacity for dispersal by both natural and human mediated mechanisms and it, along with C. fluminea, will become a major macrofouler of power 25 station water systems and other raw water systems.

The conventional control for both C. fluminea and D. polymorpha in water systems primarily involves 30 constant application of chlorine in free residual level of about 0.3 to 0.5 ppm. Even at these levels, continuous chlorination may not exclude mollusc and the presence of chlorine enhances corrosion rates. Additionally, chlorination is under close regulatory 35 scrutiny in many areas. More recently, a number of nonoxidizing toxicants, typically known as biocides, have been used as molluscicides. The prior art is

composed primarily of many different types of toxic and persistent organic compounds, for example, thiocarbonates are common. Some aromatic (i.e. benzene ring) quaternary amine and cyanide

5 molluscicides are known, but these compounds are also toxic to non-target aquatic species at or below their effective concentrations for mollusc control. Also, these compounds are often resistant to biodegradation and may not be well suited for application to potable  
10 water supplies. Further, some of the prior art, i.e. aromatic compounds, may persist in the environment and not be readily biodegradable. Therefore, there is a need to develop effective, environmentally acceptable, non-oxidizing molluscicides for control  
15 of bi-valve macrofouling.

Moreover, it would be desirable to provide such molluscicides which can be used at concentrations which can, on the one hand, control the proliferation of the molluscs, but on the other hand, be effective  
20 for that use at concentrations which have a substantially lower impact for non-target species to improve their environmental acceptability and to further be suitable for potable applications. Many conventional oxidizing and non-oxidizing biocides

25 which are utilized are so active by environmental protection standards, that they often require detoxification treatment to support their use. A molluscicide which does not require detoxification treatment would therefore be desired.

30 It is therefore an object of the present invention to provide a method for controlling proliferation of molluscs by applying a class of chemicals to this habitat which have been found to be effective to control their proliferation, particularly of D.  
35 polymorpha and C. fluminea, at effective amounts

which are below toxicity levels, which are biodegradable and which are more acceptable for potable water systems.

It is a further object of the present invention to

5 provide a method for controlling proliferation of molluscs utilizing chemicals which, in addition to their molluscicide activity, have a chemical effect on byssal attachment of molluscs as an additional macrofouling control mechanism.

10 These and other objects will be apparent from the following description and from the practice of the invention.

#### SUMMARY OF THE INVENTION

The present invention provides a method for

15 controlling and mitigating macrofouling by molluscs, particularly D. polymorpha and C. fluminea which are present in the waters in the system in which macrofouling inhibition is required, treating these waters with a mollusc proliferation-controlling

20 amount of composition comprising one, or a mixture of compounds, selected from the group consisting essentially of amines, ethoxylated amines, non-aromatic quaternary amines, ethoxylated non-aromatic quaternary amines and cyclic amines. Preferred

25 embodiments of use of such compounds are disclosed. The dosage of the composition required to effectively control the proliferation of the molluscs may be as low as about 1.0 mg/liter and up to as much as about 20 mg/liter depending on the selected treatment

30 regime. Effective treatment regimes include, but are not limited to continuous low level applications, discontinuous or intermittent applications of low to medium concentrations, and higher level slug type

treatments. These variations may be practiced under static or flowing conditions. The present invention provides control through mortality of the molluscs, by control of their attachment to, and by their 5 detachment from substrates.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Particularly preferred amines include aliphatic amines, fatty amines, their amine salts; and non-aromatic quaternary amines. Preferred aliphatic 10 amines may have alkyl or aryl groups ranging from about C<sub>2</sub> to C<sub>22</sub> which may include ethoxylated or propoxylated derivatives thereof. Cyclic amines, may be hydroxylated or ethoxylated imidazolines or other cyclic amines.

15 Exemplary non-aromatic quaternary amines and ethoxylated non-aromatic quaternary amines which are effective at application rates which are less toxic to non-target aquatic species than prior art aromatic quaternary amine molluscicides, include

20 polyethoxylated fatty amines. A particularly preferred class of quaternary amines include the chemicals sold under the trademark of Ethoquad by Akzo Chemicals Inc. A particularly preferred quaternary amine is Ethoquad C/12-75 which is a

25 cocoalkylmethyl ethoxylate of a quaternary ammonium salt. Further exemplary quaternary amines include methylated coco derivatives. A particularly preferred class of quaternary amines include the chemicals sold under the trademark of Arquad by Akzo

30 Chemicals Inc. A particularly preferred quaternary amine is Arquad 2C-75 which is a dicocodimethyl- ammonium chloride.

Exemplary fatty amines include aliphatic amines and ethoxylated aliphatic amines. A particularly preferred class of fatty amines includes chemicals sold under the trademark of Duomeen, Ethomeen and

5 Ethoduomeen by Akzo Chemicals Inc. Particularly preferred fatty amines include Duomeen C which is an N-Alkyl propane diamine, Ethomeen 0/12 which is an ethoxylated tertiary oleylamine and Ethoduomeen T/13 which is an ethoxylated N-tallow fatty diamine.

10 Exemplary cyclic amines include imidazolines and aliphatic amines of coco and oleic hydrophobes. Particularly preferred classes of imidazolines includes chemicals sold under the trademark of Alkazine by Alkaril Chemicals and the trademark of

15 Monazoline by Mona Industries Inc. Particularly preferred imidazolines include Alkazine C which is a Coco hydroxyethyl imidazoline, by Alkaril, and Monazoline O which is a substituted oleic acid imidazoline, a cyclic tertiary amine, by Mona.

20 The present invention provides a method for controlling the proliferation of mollusc in a target habitat comprising the step of periodically or continuously applying to this habitat a composition comprising one, or a mixture of two or more, of the

25 above-identified compounds. The amine compounds according to the present invention, are characterized by their properties as salts, their aliphatic hydrophobes and ethoxylated and propoxylated derivatives thereof.

30 It is well known that cationic amine compounds may exhibit general toxicity or biocide properties, particularly aromatic quaternary amines and compounds containing thiocarbonates and cyanides, which are exemplary of the prior art. This general toxicity

often exists at or below the use concentrations as molluscicides. Furthermore, many of these compounds give rise to biodegradation issues.

The compounds of the present invention are

5 distinguishable from the prior art by the virtue of their aliphatic, straight chain, characteristic and the absence of benzyl groups, thiocarbonates, cyanides or other related toxicants. Therefore, this characteristic is preferred within the current  
10 invention to improve acceptability to potable applications improved biodegradability and because of their efficacy at concentrations lower than their general purpose biocide or general toxicity limits.

The exemplary compounds described herein are active  
15 as molluscicides. Aliphatic chain lengths in the range from C<sub>8</sub> to C<sub>20</sub> or higher, and mole percent ethoxylation, prooxylation and mixed ethoxylation/propoxylation in the range from 1 to 40 or higher, should all be active. The compounds utilized in  
20 accordance with the invention, may also be used in formulations with other compounds, for other desired properties, e.g., solubility, substantivity to surfaces, foam level, etc.

It will be apparent to those skilled in the art that,  
25 based on the discoveries explained herein, formulated products can be used to enhance performance in specific applications, both using molluscicides alone and with oxidizing biocides or other toxicants. Further, the efficacy of molluscicides of the current  
30 invention may be enhanced by various types of dispersants which improves distribution, solubility and penetration of the chemical compounds. Synergism of toxic molecules with various types of dispersants, surfactants and wetting agents in water systems has

been well established in the literature. Dispersants, surfactants and wetting agents reduce surface and interfacial tension, and thereby improve the ability of toxicants in water to penetrate 5 biomass. They also improve wetting of both hard surfaces, e.g. mollusc shells and biological surfaces, e.g. gills, etc., thus increasing exposure of organisms to the toxic molecules. All of these 10 effects may be expected to occur with mixtures of the molecules of this invention and common dispersants, surfactants and wetting agents. It is apparent therefore that the above-identified compounds may be administered alone or in combination with other known 15 molluscicides and various types of dispersants or carrier compounds.

#### Static Testing

To illustrate the efficacy of the compounds utilized in accordance with the present invention, specimens of Zebra mussels (*D. polymorpha*) were obtained from 20 various stations in the midwest United States and held in a 75 gallon tank, constantly aerated, refrigerated at about 50°F until utilized in the tests. Also, Asian Clams (*C. fluminea*) were obtained from various water sources in the north central Texas 25 area and were exposed to the same chemicals. The static tests were carried out at 68-73°F in a constant temperature laboratory in which the mussels were habituated for 7 days prior to any experimentation. The mussels were exposed to 30 various concentrations of various agents within the scope of the present invention in 5 gallon plastic aquaria containing 4.5 gallons of an appropriate medium. Water in the test aquaria was constantly aerated and circulated. Media in the tanks were made 35 by mixing appropriate concentrated stock solutions of the agents with dechlorinated tap water. Control

tanks contained only the dechlorinated city water. Individual mussels of sizes ranging from recently settled juveniles, less than 1 centimeter long, to adults several years old, greater than 2.5 5 centimeters long, were tested. Samples of mussels (n = 15 individuals per dish, 30 individuals in 2 dishes per tank, 210 mussels per experiment) were placed in 4x4x1 inch high glass dishes in the bottom of each 5 gallon test aquaria, initially containing 10 only the dechlorinated city water. The shells of all mussels were etched with a permanent identifying mark and their shell length measured to the nearest 0.1 mm. Individuals were held in one of these dishes for 3 days prior to experimentation in the tanks to allow 15 them to form byssal thread attachments. Another group of 15 individuals were placed in a second dish in each tank immediately prior to biocide exposure. This second group of mussels did not have time to form new byssal attachment threads before being 20 exposed to the test agent. Thus, a group of 15 attached and 15 unattached mussels were placed in each of the 7 tanks (6 experimental, 1 control). Additionally 15 adult Asian clams were placed within each tank. Immediately after placement in the tanks, 25 the appropriate amount of the chemical agent was added to achieve the desired test concentrations. Thereafter, the media in the tanks were replaced every 3 to 4 days to maintain chemical titre and to remove any waste products which could be deleterious 30 to the mussels. The behavior of the individuals, i.e., the number with open valves, normally syphoning water over the gills and the number with the valves shut were determined during each evaluation. The number of mussels attached and detached from the 35 byssus were determined for each group in the tank, by probing each individual gently with a blunt glass rod. Byssally attached individuals cannot be

displaced by gentle probing with a glass rod while unattached individuals are readily displaced. The number of living and dead individuals were determined at each observation. Dead mussels and clams were

5 identified by gently touching the siphons and exposed mantle tissues at the posterior end of each individual in each sample with a blunt tip of a glass rod. The response to such stimulation to a living individual is to immediately clamp the valve shut.

10 If no response is elicited, a second, stronger stimulation with the glass rod is given. If no valve closure response is observed after the second stimulation, an individual was considered dead. Upon death, individuals were removed from the test

15 aquaria.

Further testing was conducted using the same protocol but limiting the exposure to chemicals for 24 hours, followed by placement in clean untreated waters. These tests were designed to study latent mortality

20 in support of discontinuous treatment regimes.

Additionally, a similar protocol was employed to elicit any synergy of non-oxidizing chemicals of this invention and chlorine, a strong oxidant. In general, this potential is evidenced by the stress

25 symptoms as observed after exposure to the non-oxidizing compounds which increases susceptibility to more potent oxidizing compounds. These tests included a 24 hour exposure to the non-oxidizing molluscicide followed by either 2 or 4 hours of

30 exposure to 2.0 mg/liter chlorine. The latent mortality of zebra mussels exposed only to the molluscicide and to both the molluscicide and chlorine, was determined separately. The lack of efficacy by chlorine, for short-term exposures, is so

well documented in the open literature that duplicate tests were not justified.

The tests were conducted with successful results using those chemicals (A through G) listed in Table 1 which further discloses their physical properties.

Table 1

	<u>Classification</u>	<u>Sub Classification</u>	<u>Typical Tradename</u>	<u>Manufacturer</u>
10	1. Quaternary Amine and Ethoxylated Quaternary Amines	A. ethoxylated B. dialkyl quat Ethoxylated Quaternary Amines	Ethoquad C/12-75 Arquad 2C-75	AKZO AKZO
15	2. Amines and Ethoxylated Amines	C. ethoxylated diamine D. ethoxylated tertiary amine E. diamine	Ethoduomeen T/13 Ethomeen 0/12 Duomeen C	AKZO AKZO AKZO
20	3. Cyclic Amines and Imidazolines	F. hydroxyethyl imidazoline G. cyclic tertiary imidazoline	Alkazine C Monozoline O	Alkaril Mona

25 Efficacy Against Attached Adult *D. polymorpha*  
 Chemicals within all the group classifications demonstrated excellent efficacy against attached *D. polymorpha* as shown in Table 2. These chemicals could be ranked by their performance in the order

30 C>E>F>A>B>G>D. In general, the diamines and ethoxylated diamines provided superior efficacy against attached *D. polymorpha* followed by the imidazoline, ethoxylated quaternary amines and quaternary amines. Both the cyclic tertiary amine

35 and ethoxylated tertiary amine provided lower efficacy.

Table 2

Efficacy Against Attached *D. polymorpha*

## 2A. Cumulative Mortality for Continuous Chemical Exposure

	Chemical	Days of Observation						
		1	2	3	4	5	6	7
5	Controls	0	0	0	0	0	0	0
	A <sub>25</sub>	0	0	0	0	0	0	0
	A <sub>1</sub>	0	0	0	0	0	0	0
	A <sub>5</sub>	0	0	7	67	93	100	100
10	A <sub>10</sub>	0	0	13	53	100	100	100
	B <sub>5</sub>	0	0	0	67	93		
	B <sub>10</sub>	0	0	13	100	100		
	C <sub>.25</sub>	0	0	0	0	0		
	C <sub>1</sub>	0	0	0	0	0	7	7
15	C <sub>5</sub>	13	20	67	100	100	100	100
	C <sub>10</sub>	33	40	87	100	100	100	100
	D <sub>5</sub>	0	0	0	0	0		
	D <sub>10</sub>	0	0	7	40	60		
	E <sub>5</sub>	0	0	60	100	100		
20	E <sub>10</sub>	0	13	73	100	100		
	F <sub>10</sub>	0	0	53	93	100		
	G <sub>10</sub>	0	0	27	60	80		
25	A <sub>5</sub>	0	0	20	50	50	50	
	C <sub>10</sub>	0	13	33	60	67		

The subscript denotes concentration in mg/liter.

Efficacy Against Unattached Adult *D. polymorpha*

In all cases the tested chemicals demonstrated excellent and typically higher efficacy against unattached *D. polymorpha* as shown in Table 3. These chemicals could be ranked by their performance in the order C>E>A>F>B>G>D. This performance ranking is comparable to that for efficacy against attached *D. polymorpha* including the performance by chemical group classifications.

Table 3

Efficacy Against Unattached D. polymorpha

## 3A. Cumulative Mortality for Continuous Chemical Exposure

	5	Days of Observation							
		1	2	3	4	5	6	7	8
	Controls	0	0	0	0	0	0	0	0
	A <sub>25</sub>	0	0	0	0	0	0	0	0
	A <sub>1</sub>	0	0	0	7	7	7	7	7
	A <sub>5</sub>	0	33	40	93	100	100	100	100
10	A <sub>10</sub>	20	27	27	87	93	100	100	100
	B <sub>5</sub>	0	0	13	93	100			
	B <sub>10</sub>	0	7	27	93	93			
	C <sub>.25</sub>	0	0	0	0	0	0	0	7
	C <sub>1</sub>	0	0	0	7	7	7	7	13
15	C <sub>5</sub>	13	53	80	87	100	100	100	100
	C <sub>10</sub>	20	40	100	100	100	100	100	100
	D <sub>5</sub>	0	0	0	7	7			
	D <sub>10</sub>	0	7	20	67	80			
	E <sub>5</sub>	0	27	87	100	100			
20	E <sub>10</sub>	0	47	100	100	100			
	F <sub>10</sub>	0	0	40	93	100			
	G <sub>10</sub>	0	0	40	93	100			

3B. Latent Mortality (Percent) After  
24 Hours Chemical Exposure

25	C <sub>10</sub>	0	53	87	93	93		
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The subscript denotes concentration in mg/liter.

Efficacy Against Adult C. fluminea

Chemical C demonstrated superior efficacy against C. fluminea, as shown in Table 4. Chemicals E and F followed with good to excellent efficacy. The overall performance against C. fluminea follows the order C>E>F>G>B>D.

Table 4

Efficacy Against C. fluminea4A. Cumulative Percent Mortality  
for Continuous Chemical Exposure

5	Chemical	Days of Observation							
		1	2	3	4	5	6	7	8
	Controls 0	0	0	0	0	0	0	0	0
10	B <sub>5</sub>	0	0	0	0	7			
	B <sub>10</sub>	0	0	0	7	7			
	C <sub>.25</sub>	0	0	7	7	13	13	13	13
	C <sub>1</sub>	0	0	0	7	53	60	67	67
	C <sub>5</sub>	0	7	47	67	73	73	100	100
	C <sub>10</sub>	0	7	67	73	80	86	93	100
15	D <sub>5</sub>	0	0	0	0	0			
	D <sub>10</sub>	0	0	0	0	7			
	E <sub>5</sub>	0	0	0	43	79			
	E <sub>10</sub>	0	0	7	53	80			
	F <sub>10</sub>	0	0	7	33	53			
	G <sub>10</sub>	0	0	0	0	53			
20	4B. Latent Mortality (Percent) After 24 Hours Chemical Exposure								
	C <sub>10</sub>	0	0	0	73	80			

The subscript denotes concentration in mg/liter.

The order of performance follows that seen against  
25 D. polymorpha but with generally lower efficacies.  
This difference is explained by the greater ability  
of C. fluminea to avoid noxious chemicals.

#### Syphon and Feeding Activity

Observation of altered syphoning activity was  
30 recorded daily. These observations are useful to  
determine sublethal responses to various  
concentrations of chemicals. In general, D.  
polymorpha exhibited less avoidance of chemical  
exposure than did C. fluminea which is useful to  
35 understand differences in efficacy. When combined  
with other stress indicating observations it will be

apparent to those skilled in the art that impairing the mollusc's ability to avoid chemical exposure renders it susceptible to synergistic treatments with toxicants such as chlorine.

5 Inhibition of Attachment

Unattached D. polymorpha were placed into chemically treated environments at various concentrations and their natural response to attach to available substratum was observed and recorded. The results 10 are shown in Table 5. These observations are most useful in a preventive control treatment regime. Many of the chemicals exhibited excellent control.

Table 5

5A. Percent Inhibition of Attachment for D. polymorpha

15	<u>Chemical</u>	<u>Days of Observation</u>							
		1	2	3	4	5	6	7	8
	Controls	>20	>20	>20	>20	>20	>20	>20	>20
	A <sub>.25</sub>	8	8	8	0	0	0	0	0
	A <sub>1</sub>	27	20	20	20	22	14	7	0
20	A <sub>5</sub>	93	87	100	100	100			
	A <sub>10</sub>	100	100	100	100	100			
	B <sub>5</sub>	100	100	100	100	100			
	B <sub>10</sub>	100	27	100	100	100			
	C <sub>.25</sub>	33	40	40	20	20	20	20	13
25	C <sub>1</sub>	0	0	0	7	7	7	7	13
	C <sub>5</sub>	87	92	100	100	100			
	C <sub>10</sub>	93	100	100					
	D <sub>5</sub>	93	80	67	60	100			
	D <sub>10</sub>	93	93	100	100	100			
30	E <sub>5</sub>	100	100	100	100	100			
	E <sub>10</sub>	100	100	100	100	100			
	F <sub>10</sub>	93	100	100	100	100			
	G <sub>10</sub>	100	100	100	100	100			

5B. Latent Mortality (Percent) After  
35 24 Hours Chemical Exposure

C <sub>10</sub>	93	80	100	100	100
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The subscript denotes concentration in mg/liter.

Synergy with Oxidizing Biocides

The testing for synergy of the current invention, which employs non-oxidizing chemicals, and conventionally applied oxidizing biocides produced 5 positive results. Further, these results are consistent with the increased susceptibility to noxious chemicals as observed in the stress indications of specimens treated by current invention.

10 The data for synergy between Chemical A and chlorine is presented in Table 6. The effect is seen as acceleration of time to death and overall higher mortalities. Regimes which repeat this cycle of chemical exposure are expected to produce more ideal 15 results.

Table 6

## Synergy of Amines and Oxidizing Biocides

	<u>Day of Observation</u>					
	1	2	3	4	5	6
20	Chemical A5 - 24 Hours	0	0	20	50	50
	Chemical A5 - 24 Hours plus 2 Hrs.	0	70	70	70	70
25	Chlorine(2)					
	Chemical A5 - 24 Hours plus 2 Hrs. Chlorine(2)	0	40	50	70	70
30	Notes:	The subscript denotes concentration in mg/liter				

Summary of Chemical Performance

This invention provides a wide range of chemicals, having various classifications, which work 35 effectively to perform one or more effects which are

important to mollusc control. The side-by-side comparison of the tested chemicals and their effect(s) is presented in Table 7. From this presentation, those skilled in the art will be able 5 to select the desired effects from one or a combination of the chemicals tested and to be more effective against each species of mollusc.

Table 7  
Performance Comparison of All Chemicals

	10	Chemical	Sub Classification	M1	M2	M3	A
		A	ethoxylated quaternary amine	4	3	-	1
15	B		quaternary amine	5	5	5	1
	C		ethoxylated diamine	1	1	1	1
20	D		ethoxylated tertiary amine	7	7	6	1
	E		diamine	2	2	2	1
	F		imidazoline	3	4	3	1
25	G		cyclic tertiary imidazoline	6	6	4	1

Notes:

M1 = Mortality against attached D. polymorpha  
 M2 = Mortality against unattached D. polymorpha  
 M3 = Mortality against C. fluminea  
 30 A = Control of attachment  
 1 = Highest Performance  
 7 = Lowest Performance

It will be apparent to those skilled in the art that there are various applications for the method of the 35 present invention which include, but are not limited

to, control and mitigation of macrofouling of molluscs in various aqueous systems such as fresh and saline water supplies used for industrial, steam, electric, municipal and similar applications where

5 macrofouling may cause impairment of system performance. Specific water systems which may be protected according to the method of the present invention include, but are not limited to, once-through and recirculating cooling waters, potable

10 water systems, fire protection systems and other types of auxiliary water systems.

## WHAT IS CLAIMED:

1. A method for controlling the proliferation of molluscs in a target habitat comprising the step of applying to said habitat a mollusc proliferation-controlling effective amount of a compound or mixture of compounds selected from the group consisting of amines, ethoxylated amines, non-aromatic quaternary amines, ethoxylated non-aromatic quaternary amines and cyclic amines.
- 10 2. A method according to Claim 1 wherein said effective amount is sufficient to inhibit proliferation of unattached molluscs in said habitat.
- 15 3. A method according to Claim 1 wherein said effective amount is sufficient to inhibit proliferation of attached molluscs in said habitat.
4. A method according to Claim 1 wherein said molluscs comprise Dreissena polymorpha.
5. A method according to Claim 1 wherein said molluscs comprise Corbicula fluminea.
- 20 6. A method according to Claim 1 wherein said effective amount is from about 1 - 20 mg/liter in said habitat.
- 25 7. A method according to Claim 1 wherein said amines comprise aliphatic amines, fatty amines, or their salts.
8. A method according to Claim 1 wherein said quaternary amines comprise a dialkyl quaternary ammonium salt.

9. A method according to Claim 1 wherein said cyclic amines comprise an imidazoline.

10. A method according to Claim 9 wherein said imidazoline is hydroxyethyl imidazoline.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/06236

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) <sup>6</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5): A01N 33/02, 33/08, 33/12, 33/14, 43/50

U.S.CI.: 514/385, 396, 401, 402, 612, 642, 643, 663, 667, 918

## II. FIELDS SEARCHED

Minimum Documentation Searched <sup>7</sup>

Classification System	Classification Symbols
U.S.	514/385, 396, 401, 402, 612, 642, 643, 663, 667 and 918.

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>

APS Queries: MOLLUSCICID? and (AMINE?)  
 " " (QUATERNARY AMMONIUM)  
 " " (? imidazoline?)

## III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup>

Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	US, A, 4,289,820 (DAVIES ET AL.) 26 May 1981	1,7
Y	See column 5, line 3 and column 6, lines 38-53.	2-6
X	US, A, 4,789,489 (HOLLIS ET AL.) 06 December 1988	1-3,5,8
Y	See column 1, lines 20-39 and column 4, lines 7-61.	4,6
Y	US, A, 4,447,411 (LANGDON) 08 May 1984 See column 5, last paragraph through column 6, lines 1-14.	1-6
Y	US, A, 4,923,887 (BAUER ET AL.) 08 May 1990 See column 1, lines 8-24.	1-7
Y	Derwent Publications LTD's Abstract of JP 61122208, 10 June 1986	1-7
P,Y	US, A, 5,030,629 (RAJADHYAKSHA) 09 July 1991 See column 3, line 63 through column 7, line 54, column 13, lines 54-57 and column 14, lines 22-36.	1-6, 9-10
Y	US, A, 4,876,249 (RAJADHYAKSHA) 24 October 1989 See column 3 lines 22 through column 4 line 43, column 12, lines 21-25 and column 12 line 58 through column 13, line 9.	1-6,9-10

\* Special categories of cited documents: <sup>10</sup>

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

06 January 1992

Date of Mailing of this International Search Report

24 JAN 1992

International Searching Authority

ISA/US

Signature of Authorized Officer

for John Pak

Nguyen Ngoc-Ho  
INTERNATIONAL DIVISION