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CONTROLLING BACTERIA WITH A FATTY TETRAAMINE

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ABSTRACT OF THE DISCLOSURE

Fatty tetraamines are used alone or in admixture with other specified compounds as biocides for various purposes.

This invention relates to fatty tetraamines and their use as biocides. More particularly, this invention relates to the use of N''',N''-di-(3-aminopropyl) aminofattyamines as biocides.

Much effort has been expended to devise a biocide which is all-purpose. Usually, the biocide is useful against one or more aerobes or anaerobes, but never all of them.

With the recent advent of difunctional fatty compounds, particularly the dicarboxylic acids, chemists and bacteriologists have come closer to such a desire. Copending patent applications, Ser. No. 41,014 filed Nov. 9, 1964, now U.S. Pat. 3,448,374 issued Dec. 24, 1968, and Ser. No. 398,437 filed Sept. 22, 1964 now U.S. Pat. 3,354,213 issued Nov. 21, 1967, respectively, are typical examples of such recent work.

Accordingly, an object of this invention is to provide diamino fatty amines which are useful as biocides.

Another object is to provide bactericides which are useful against anaerobes.

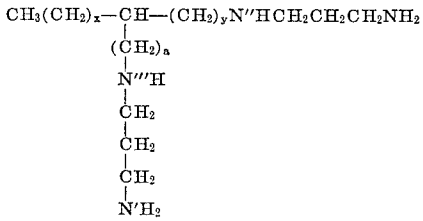
Still another object is to provide bactericides which are useful for aerobes.

A further object is to provide novel sulfate reducer bactericides.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

It has now been found that fatty tetraamines of the following formula may be used as biocides for anaerobes and aerobes:

FORMULA I



where:

a=0 to 2

x+y=6 to 22

Among the fatty tetraamines which fall within the above formula are

N''',N''-di-(3-aminopropyl)aminomethylcaprylylamine,
N''',N''-di-(3-aminopropyl)aminomethylcaprylamine,
N''',N''-di-(3-aminopropyl)aminomethyllaurylamine,
N''',N''-di-(3-aminopropyl)aminomethylmyristylamine,
N''',N''-di-(3-aminopropyl)aminomethylpalmitylamine,
N''',N''-di-(3-aminopropyl)aminomethylstearylamine,
N''',N''-di-(3-aminopropyl)aminomethylarachidylamine,
N''',N''-di-(3-aminopropyl)aminomethylbehenylamine,
N''',N''-di-(3-aminopropyl)aminomethyllignocerylamine,
N''',N''-di-(3-aminopropyl)aminoethylcaprylylamine,

N''',N''-di-(3-aminopropyl)aminoethylcaprylamine,
N''',N''-di-(3-aminopropyl)aminoethyllaurylamine,
N''',N''-di-(3-aminopropyl)aminoethylmyristylamine,
N''',N''-di-(3-aminopropyl)aminoethylpalmitylamine,
N''',N''-di-(3-aminopropyl)aminoethylstearylamine,
N''',N''-di-(3-aminopropyl)aminoethylarachidylamine,
N''',N''-di-(3-aminopropyl)aminoethylbehenylamine,
N''',N''-di-(3-aminopropyl)aminoethyllignocerylamine,

or mixtures thereof such as derivable from natural fats and oils such as tallow, soybean oil and coconut oil.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others, and the compound possessing the features, properties, and the relation of elements, which are exemplified in the following detailed disclosure, and the scope of the invention will be indicated in the claims.

Reference is now made to the following examples which illustrate the invention in detail:

EXAMPLE I

A number of known biocides and the N''',N''-di-(3-aminopropyl)aminofattyamines are compared as to their algaecidal activity against chlamydomonas (C in Table 1 which follows(and scenedesmus (S). All results shown (expressed in p.p.m.) are of replicate testing with the highest dilution exhibiting growth and the lowest dilution inhibiting growth being reported as a range. All tests are run at room temperature, the chemical named being tested on an as is basis.

TABLE 1

Chemical	Algae C	Algae S
Zinc dimethyldithiocarbamate	5.0–7.5	5.0–7.
Tributyltin oxide	10–15	10–1
Tributyltin chloride	5.0–7.5	5.0–7.5
N-alkyl(C_{12}, C_{14}, C_{16})dimethylbenzyl ammonium chloride	2.5–5.0	2.5–5.0
N-oleyltetrahydropyrimidone	<2.5	5.0–10
N-dodecyl 3,3'-imino-di-propionamide	2.5–5.0	10–20
N-[3-octadecenylamine)propyl]xylylstearamide	10–20	5–10
Copper sulfate	<0.11	<0.11
N''',N''-di-(3-aminopropyl)aminomethly-stearylamine (DMSA)	<0.11	<0.11
Glutamate salt of DMSA	0.11	0.46
Glutamate salt of N''', N''-di-(3-aminoproply) aminococoamine	0.15	0.11

EXAMPLE II

A common contaminant of oil injection systems is D-desulfricans, which is an anaerobic bacteria. In the Table 2 which follows, the named diamines and their salts (on an "as-is" basis) are compared to the named tetraamines and the results are expressed in a lower and upper effective range in a p.p.m. basis. The tests are run at 31°–32° C. for twenty-eight days in a 3.0% NaCl based media.

TABLE 2

Chemical	Effective range
N-coco trimethylene diamine (50% active)	>50 <75
Aminomethylstearylamine acetate salt	>75 <100
Aminomethylstearylamine gluconate salt	>75 <100
Aminomethylstearylamine	>50 <75
N''',N''-di-(3-aminopropyl)aminomethylstearyl-amine gluconate salt	>25 <50
N''',Ni''-di-(3-aminopropyl)aminomethylestearyl-amine	>7.5 <12.5

EXAMPLE III

N''',N''-di-(3 - aminopropyl)aminomethylstearylamine (DMSA) exhibits synergistic bactericidal activity when employed in combination with a compound selected from

the group consisting of dimethylsulfoxide (DMSO) and the benzyl quaternary of dimethyl tertiary β-amine (BQDβA).

Following are the test data showing activity against both aerobic and anaerobic bacteria in water and in brine.

TABLE 3

Compound	Organism tested	Diluent	Minimum killing dose (p.p.m.)
DMSA (100%)	*Pseudomonas aeruginosa*	Distilled H_2O	10
	Aerobacter aerogenes [1]		10
	Staphyloccoccus aureus		10
	Bacillus cereus		5
	D. desulfuricans (S-R [2])		10
BQDβA	*Pseudomonas aeruginosa*		>200
	Aerobacter aerogenes		10
	Staphylococcus aureus		10
	D. desulfuricans (S-R [2])		10
DMSO (100%)	Sulfate-reducers [2]	Distilled H_2O	>100
DMSA (37.5%)		Brine	>100
DMSO (12.5%)		H_2O	<1
DMSA (37.5%)		Brine	20
BQDβA(12.5%)		H_2O	<1
QD β (12.5%)	do.[2]	Brine	10
DMSA (37.5%)	*Aerobacter aerogenes*	Brine	20
DMSO (12.5%)	*Pseudomonas aeruginosa*		10
Water (50%)			
DMSA (50%)	*Aerobacter aerogenes*	Brine	>80
Water (50%)	*Pseudomonas aeruginosa*		>80
DMSO (100%)	*Aerobacter aerogenes*		>80
	Pseudomonas aeruginosa		>80
BQDβA (100%)	*Aerobacter aerogenes*		>80
	Pseudomonas aeruginosa		>80

[1] Exposure bottles containing sterile distilled water or sterile 3% synthetic brine are inoculated with the test organisms (aerobes)-(slime formers) to make up a concentration of 200,000 organisms/ml. diluent (previously determined by plate counts). The chemical compounds are added to the exposure bottles at appropriate doses for 1 or 2 hours as indicated. After the exposure time, a 1 ml. sample from each bottle is transferred to Difco's sterile nutrient broth bottles and incubated at 37° C. for 7-8 days. Growth is determined by turbidity in the broth and cidal effects are determined by subculturing in neutralizing broth and also by biochemical measurement of cell viability.

[2] Inhibition of *D. desulfuricans* (sulfate-reducers) is determined by the procedure recommended by the American Petroleum Industry (1959). Exposure bottles containing either sterile distilled water or sterile 3% synthetic brine are inoculated with four day old cultures of *D. desulfuricans* in an anaerobic condition and exposed to the chemical compounds at appropriate doses for 1 or 2 hours as indicated. After the exposure time, a 1 ml. sample from each bottle is transferred to an anaerobic sulfate-reducing medium (API broth) and incubated at 37° C. for 15-20 days. Growth of sulfate-reducers in the bottles is indicated by blackening of the medium (red to black iron sulfide).

EXAMPLE IV

N‴,N″-di-(3 - aminopropylaminomethylstearylamine (DMSA) and homologs are very effective in controlling aerobic bacteria which are common contaminants in oil wells, cooling towers and swimming pools, as evidenced by the data of Table 4. All tests are run for 24 hours at 37° C.

TABLE 4

	P [1] p.p.m.	E [2] p.p.m.	S [3] p.p.m.	B [4] p.p.m.
DMSA (100% active)	5-10	5-10	5-10	2. 5-5. 0
N-cocotrimethylene diamine	5-100	50-75	50-75	25-50
Alkyl dimethyl ethyl benzyl [5] ammonium chloride / Alkyl dimethylbenzyl ammonium chloride	100	100	100	100

[1] P=*Pseudomonas aeruginosa.*
[2] E=*E. coli.*
[3] S=*Staphylococcus aureus.*
[4] B=*Bacillus cereus v. mycoides.*
[5] Equal parts.

The above data establishes that N‴, N″-di-(3-aminopropyl) aminomethylstearylamine is good as a microbiological control in industrial water systems and waterflood injection systems. It is also good as a microbioligical control in water-base mud systems as related to drilling and completion fluids where there is a high concentration of aerobic and anaerobic organisms. For disinfecting floors in hospitals, T.B. sanitariums, industries, gymnasiums, or home cellars where airborne micro-organisms may grow, AMSA is also effective. And, in dilute form, it would probably be good as an additive to some textiles or leather materials. It also functions as a paint preservative for water-base paints where there may be as incidence of protein-decomposing bacteria.

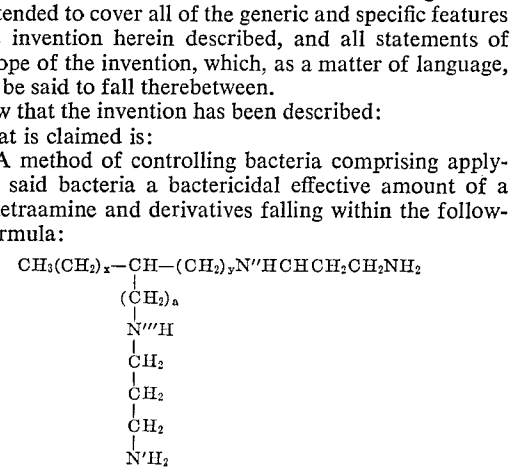
It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained, and, since certain changes may be made in carrying out the above method and in the compounds set forth without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention, which, as a matter of language, might be said to fall therebetween.

Now that the invention has been described:

What is claimed is:

1. A method of controlling bacteria comprising applying to said bacteria a bactericidal effective amount of a fatty tetraamine and derivatives falling within the following formula:



where

a=0 to 2

$x+y$=6 to 22.

2. The method of claim **1** wherein 0.1 to 500 p.p.m. solution of said tetraamine is utilized.

3. The method of claim **1** wherein the tetraamine used is N‴,N″-di-(3-aminopropyl) aminomethylstearylamine.

References Cited

UNITED STATES PATENTS

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3,418,374	12/1968	Miller	260—583I

JEROME D. GOLDBERG, Primary Examiner