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(54) **Title**: MICROBICIDAL COMPOSITION COMPRISING 2-DECYLTHIOETHYLAMINE

(57) **Abstract**: A synergistic microbicidal composition having two components. The first component is a nonionic surfactant with structure: $R^1O(CH_2CH(CH_3)O)_5(CH_2CH_2O)_9H$, where $R^1$is a C_8alkyl group. The second component is 2-decylthioethylamine. The weight ratio of the nonionic surfactant to 2-decylthioethylamine is from 1:0.004 to 1:0.0137 or 1:0.016 to 1:0.4571. Alternatively, the first component is a nonionic surfactant with structure: $R^2O(CH_2CH(CH_3)O)_3(CH_2CH_2O)_7H$, where R^2 is a mixture of C_8-C_{14} linear alkyl groups. The second component is 2-decylthioethylamine. In this case, the weight ratio of the nonionic surfactant to 2-decylthioethylamine is from 1:0.0023 to 1:0.4571.

MICROBICIDAL COMPOSITION

This invention relates to microbicidal compositions containing 2-decylthioethylamine and a surfactant.

A composition containing 5-chloro-2-methylisothiazolin-3-one, 2-methylisothiazolin-3-one and a nonionic dispersant is disclosed in U.S. Patent No. 4,295,932. The composition contains a 3:1 mixture of 5-chloro-2-methylisothiazolin-3-one and 2-methylisothiazolin-3-one, and a copolymer of ethylene oxide and propylene oxide which appears to have the same composition as PLURONIC L61 or TERGITOL L61 dispersant. However, there is a need for combinations of microbicides having synergistic activity against various strains of microorganisms to provide effective control of the microorganisms. Moreover, there is a need for such combinations containing lower levels of individual microbicides for environmental and economic benefit. The problem addressed by this invention is to provide such synergistic combinations of microbicides.

STATEMENT OF THE INVENTION

The present invention is directed to a synergistic microbicidal composition comprising: (a) a nonionic surfactant with structure:

$$R^1O(CH_2CH(CH_3)O)_5(CH_2CH_2O)_9H$$

where R^1 is a C_8 alkyl group; and (b) 2-decylthioethylamine; wherein a weight ratio of said nonionic surfactant to 2-decylthioethylamine is from 1:0.004 to 1:0.0137 or 1:0.016 to 1:0.4571.

The present invention is further directed to a synergistic microbicidal composition comprising: (a) a nonionic surfactant with structure:

$$R^2O(CH_2CH(CH_3)O)_3(CH_2CH_2O)_7H$$

where R^2 is a mixture of C_8-C_{14} linear alkyl groups; and (b) 2-decylthioethylamine; wherein a weight ratio of said nonionic surfactant to 2-decylthioethylamine is from 1:0.0023 to 1:0.4571.

The present invention is further directed to a synergistic microbicidal composition comprising: (a) a nonionic surfactant with structure:

$$R^2O(CH_2CH(CH_3)O)_3(CH_2CH_2O)_5H$$

where R^2 is a mixture of C_8-C_{14} linear alkyl groups; and (b) 2-decylthioethylamine; wherein a weight ratio of said nonionic surfactant to 2-decylthioethylamine is from 1:0.0023 to 1:0.3657.

The present invention is further directed to methods for inhibiting the growth of microorganisms in aqueous media by adding to an aqueous medium a nonionic surfactant as described herein and 2-decylthioethylamine in the ratios described herein.

DETAILED DESCRIPTION OF THE INVENTION

"DTEA" is 2-decylthioethylamine, CAS No. 29873-30-1, or its salts. DTEA may be present in the form of a salt, especially the hydrochloride salt; ratios and amounts stated herein including 2-decylthioethylamine are based on the hydrochloride salt. As used herein, the following terms have the designated definitions, unless the context clearly indicates otherwise. The term "microbicide" refers to a compound capable of inhibiting the growth of or controlling the growth of microorganisms; microbicides include bactericides, fungicides and algaecides. The term "microorganism" includes, for example, fungi (such as yeast and mold), bacteria and algae. The following abbreviations are used throughout the specification: ppm = parts per million by weight (weight/weight), mL = milliliter. Unless otherwise specified, temperatures are in degrees centigrade (°C), references to percentages are percentages by weight (wt%) and amounts and ratios are on an active ingredient basis, i.e., total weight of DTEA and the nonionic surfactant. Numbers of polymerized units of propylene oxide or ethylene oxide are number averages.

Preferably, the weight ratio of the nonionic surfactant with structure:

$$R^1O(CH_2CH(CH_3)O)_5(CH_2CH_2O)_9H$$

where R^1 is a C_8 alkyl group to 2-decylthioethylamine is from 1:0.016 to 1:0.4571, preferably from 1:0.032 to 1:0.4571. Preferably, the weight ratio of the nonionic surfactant with structure:

$$R^2O(CH_2CH(CH_3)O)_3(CH_2CH_2O)_7H$$

where R^2 is a mixture of C_8-C_{14} linear alkyl groups to 2-decylthioethylamine is from 1:0.01 to 1:0.4571. Preferably, the weight ratio of the nonionic surfactant with structure:

$$R^2O(CH_2CH(CH_3)O)_3(CH_2CH_2O)_5H$$

where R^2 is a mixture of C_8-C_{14} linear alkyl groups to 2-decylthioethylamine is from 1:0.02 to 1:0.3657, preferably from 1:0.0343 to 1:0.3657.

The present invention is further directed to a method for inhibiting the growth of mold, preferably *A. niger*, in an aqueous medium by adding: (a) a nonionic surfactant with structure:

$$R^2O(CH_2CH(CH_3)O)_3(CH_2CH_2O)_7H$$

where R^2 is a mixture of C_8-C_{14} linear alkyl groups; and (b) 2-decylthioethylamine; wherein a weight ratio of said nonionic surfactant to 2-decylthioethylamine is from 1:0.01 to 1:0.4571.

The present invention is further directed to a method for inhibiting the growth of mold, preferably *A. niger*, in an aqueous medium by adding: (a) a nonionic surfactant with structure:

$$R^1O(CH_2CH(CH_3)O)_5(CH_2CH_2O)_9H$$

where R^1 is a C_8 alkyl group; and (b) 2-decylthioethylamine; wherein a weight ratio of said nonionic surfactant to 2-decylthioethylamine is from 1:0.032 to 1:0.4571.

The present invention is further directed to a method for inhibiting the growth of mold, preferably *A. niger*, in an aqueous medium by adding: (a) a nonionic surfactant with structure:

$$R^2O(CH_2CH(CH_3)O)_3(CH_2CH_2O)_5H$$

where R^2 is a mixture of C_8-C_{14} linear alkyl groups; and (b) 2-decylthioethylamine; wherein a weight ratio of said nonionic surfactant to 2-decylthioethylamine is from 1:0.02 to 1:0.3657, preferably from 1:0.0343 to 1:0.3657.

R^2 is a mixture of C_8-C_{14} linear alkyl groups. Preferably, the C_8-C_{14} linear alkyl groups comprise from 50 to 85 wt% C_8-C_{10} linear alkyl groups and 15 to 50 wt% C_{12}-C_{14} linear alkyl groups, preferably from 60 to 75 wt% C_8-C_{10} linear alkyl groups and 25 to 40 wt% C_{12}-C_{14} linear alkyl groups, preferably about 70 wt% C_8-C_{10} linear alkyl groups and about 30 wt% C_{12}-C_{14} linear alkyl groups. Preferably, the linear alkyl groups are derived from seed oil. Preferably, R^1 is 2-ethylhexyl.

Preferably, each of the compositions is substantially free of microbicides other than the nonionic surfactant and DTEA, i.e., it has less than 1 wt% of microbicides other than the nonionic surfactant and DTEA based on total weight of active ingredients, preferably less than 0.5 wt%, preferably less than 0.2 wt%, preferably less than 0.1 wt%. Preferably, when the nonionic surfactant and DTEA are added to an aqueous medium, the medium is substantially free of other microbicides, i.e., it has less than 1 wt% of microbicides other than the nonionic surfactant and DTEA based on total weight of active ingredients, preferably less than 0.5 wt%, preferably less than 0.2 wt%, preferably less than 0.1 wt%.

The compositions of this invention may contain other ingredients, e.g., defoamers and emulsifiers. The microbicidal compositions of the present invention can be used to inhibit the growth of microorganisms or higher forms of aquatic life (such as protozoans, invertebrates, bryozoans, dinoflagellates, crustaceans, mollusks, etc) by introducing a microbicidally effective amount of the compositions into an aqueous medium subject to

microbial attack. Suitable aqueous media are found in, for example: industrial process water; electrocoat deposition systems; cooling towers; air washers; gas scrubbers; mineral slurries; wastewater treatment; ornamental fountains; reverse osmosis filtration; ultrafiltration; ballast water; evaporative condensers; heat exchangers; pulp and paper processing fluids and additives; starch; plastics; emulsions; dispersions; paints; latices; coatings, such as varnishes; construction products, such as mastics, caulks, and sealants; construction adhesives, such as ceramic adhesives, carpet backing adhesives, and laminating adhesives; industrial or consumer adhesives; photographic chemicals; printing fluids; household products, such as bathroom and kitchen cleaners; cosmetics; toiletries; shampoos; soaps; personal care products such as wipes, lotions, sunscreen, conditioners, creams, and other leave-on applications; detergents; industrial cleaners; floor polishes; laundry rinse water; metalworking fluids; conveyor lubricants; hydraulic fluids; leather and leather products; textiles; textile products; wood and wood products, such as plywood, chipboard, flakeboard, laminated beams, oriented strandboard, hardboard, and particleboard; petroleum processing fluids; fuel; oilfield fluids, such as injection water, fracture fluids, and drilling muds; agriculture adjuvant preservation; surfactant preservation; medical devices; diagnostic reagent preservation; food preservation, such as plastic or paper food wrap; food, beverage, and industrial process pasteurizers; toilet bowls; recreational water; pools; and spas.

The specific amount of the microbicidal compositions of this invention necessary to inhibit or control the growth of microorganisms in an application will vary. Typically, the amount of the composition of the present invention is sufficient to control the growth of microorganisms if it provides from 1 to 500 ppm (parts per million) active ingredients of the composition. It is preferred that the active ingredients (i.e., nonionic surfactant and DTEA) of the composition be present in the medium to be treated in an amount of at least 3 ppm, preferably at least 5 ppm, preferably at least 10 ppm. It is preferred that the active ingredients of the composition be present in the locus in an amount of no more than 400 ppm, preferably no more than 300 ppm, preferably no more than 200 ppm, preferably no more than 100 ppm, preferably no more than 80 ppm, preferably no more than 70 ppm. In a method of this invention, a composition is treated to inhibit microbial growth by adding, together or separately, the nonionic surfactant and DTEA, in amounts that would produce the concentrations indicated above.

EXAMPLES

Surfactants and biocides were evaluated for synergy by determining the synergy index (S.I.) of the combination. Synergy index was calculated based on minimum inhibitory concentrations (MIC) of two antimicrobial compounds (A and B) alone and in combinations. The tests organisms were Gram negative bacteria (*Pseudomonas aeruginosa* ATCC # 15442), Gram positive bacteria (*Staphylococcus aureus ATCC #* 6538), yeast (*Candida albicans* ATCC#10203) and mold (*Aspergillus niger* ATCC# 16404). Contact time for the bacteria was 24 and 48 hours, yeast was 48 and 72 hrs, and 3 and 7 days for mold. The test was carried out in 96 well microtiter plates.

Surf. A $R^1O(CH_2CH(CH_3)O)_5(CH_2CH_2O)_9H$, where R^1 is 2-ethylhexyl

Surf. D $R^2O(CH_2CH(CH_3)O)_3(CH_2CH_2O)_5H$

Surf. E $R^2O(CH_2CH(CH_3)O)_3(CH_2CH_2O)_7H$

In Surf. D and Surf. E, R^2 is a mixture of C_8-C_{14} linear alkyl groups (70% C_8-C_{10} linear alkyl and 30% C_{12}-C_{14} linear alkyl)

Inoculums Used

Inoculum Size of organisms (CFU/ml)				
Surfactants	*Staphylococcus aureus* ATCC# 6538	*Pseudomonas aeruginosa* ATCC # 15442	*Aspergillus niger* ATCC# 16404	*Candida albicans* ATCC#10203
Surf. A	1.156E+06	8.134E+07	1.156E+06	1.156 +06
Surf. D	1.808E+05	1.156E+08	1.156E+06	5.726E+05
Surf. E	1.808E+06	5.727E+07	5.726E + 05	1.808E + 06

Table4. Media Used

Media Used for testing			
Staphylococcus aureus ATCC# 6538	*Pseudomonas aeruginosa* ATCC # 15442	*Aspergillus niger* ATCC# 16404	*Candida albicans* ATCC#10203
10% Tryptic soy broth	10% Tryptic soy broth	Potato dextrose broth	Potato dextrose broth

The pH of the Triptic soy broth was 7.3 and the Potato dextrose broth was 5.1.

The test results for demonstration of synergy of the MIC combinations are shown in the tables below. Each table shows the results for combinations of two components against the microorganisms tested with incubation times; the end-point activity in ppm measured by the MIC for compound A alone (CA), for component B alone (CB), and the mixture (Ca) and

(Cb); the calculated SI value; and the range of synergistic ratios for each combination tested. SI is calculated as follows:

$$Ca/CA + Cb/CB = \text{Synergy Index ("SI")}$$

Wherein:

CA = concentration of compound A in ppm, acting alone, which produced an end point (MIC of Compound A).

Ca = concentration of compound A in ppm, in the mixture, which produced an end point.

CB = concentration of compound B in ppm, acting alone, which produced an end point (MIC of Compound B).

Cb = concentration of compound B in ppm, in the mixture, which produced an end point.

When the sum of Ca/CA and Cb/CB is greater than one, antagonism is indicated. When the sum is equal to one, additivity is indicated, and when less than one, synergism is demonstrated.

The ratio ranges at which DTEA (in the form of its hydrochloride salt) and the surfactants were tested are as summarized in the following tables:

DTEA with Surf. A				
Organism	ATCC#	From	To	Ratio Range
Staphylococcus aureus	6538	0.02:20,000	100:218.75	1:0.000001 - 1:0.45714
Aspergillus niger	16404	0.2:20,000	1,000:218.75	1:0.00001 - 1:4.5714
Candida albicans	10203	0.2:20,000	1,000:218.75	1:0.00001 - 1:4.5714
Pseudomonas aeruginosa	15442	0.2:20,000	1,000:218.75	1:0.00001 - 1:4.5714

DTEA with Surf. E				
Organism	ATCC#	From	To	Ratio Range
Staphylococcus aureus	6538	0.02:20,000	100:218.75	1:0.000001 - 1:0.45714
Aspergillus niger	16404	0.2:20,000	1,000:218.75	1:0.00001 - 1:4.5714
Candida albicans	10203	0.2:20,000	1,000:218.75	1:0.00001 - 1:4.5714
Pseudomonas aeruginosa	15442	0.02:20,000	100:218.75	1:0.000001 - 1:0.45714

DTEA with Surf. D				
Organism	ATCC#	From	To	Ratio Range
Staphylococcus aureus	6538	0.02:20,000	100:218.75	1:0.000001 - 1:0.45714
Aspergillus niger	16404	0.02:20,000	100:218.75	1:0.000001 - 1:0.45714
Candida albicans	10203	0.2:20,000	1,000:218.75	1:0.00001 - 1:4.5714
Pseudomonas aeruginosa	15442	0.02:20,000	100:218.75	1:0.000001 - 1:0.45714

A:Surf. A
B:DTEA
Media: 1/10 TSB
Inoculum size:8.13E+07
P. aeruginosa ATCC#15442 **No Synergy**

A:Surf. A
B:DTEA
Media: PDB
Inoculum size:1.156E+06

	PPM AI MIC Values (3rd day)				S.I.	Ratio (Ca: Cb)
Test	Alone		Combination			
Organism	CA	CB	Ca	Cb		
A.niger	>20000	200	2500	80	**<0.53**	1:0.0320
ATCC#16404	>20000	200	2500	100	**<0.63**	1:0.0400
	>20000	200	1750	80	**<0.49**	1:0.0457
	>20000	200	1750	100	**<0.59**	1:0.0571
	>20000	200	875	100	**<0.54**	1:0.1143
	>20000	200	437.5	100	**<0.52**	1:0.2286
	>20000	200	218.75	100	**<0.51**	1:0.4571

A:Surf. A
B:DTEA
Media: PDB
Inoculum size:1.156E+06

	PPM AI MIC Values (48hrs)				S.I.	Ratio (Ca: Cb)
Test	Alone		Combination			
Organism	CA	CB	Ca	Cb		
C.albicans	>20000	50	2500	40	**<0.93**	1:0.0160
ATCC#10203	>20000	50	1750	40	**<0.89**	1:0.0229
	>20000	50	875	40	**<0.84**	1:0.0457

A:Surf. A
B:DTEA
Media: 1/10 TSB
Inoculum size:1.156E+06

	PPM AI MIC Values (24hrs)				S.I.	Ratio (Ca: Cb)
Test	Alone		Combination			
Organism	CA	CB	Ca	Cb		
S.aureus	>20000	4	2500	1	**<0.38**	1:0.0004
ATCC# 6538	>20000	4	2500	2	**<0.63**	1:0.0008
	>20000	4	2500	3	**<0.88**	1:0.0012
	>20000	4	1750	1	**<0.34**	1:0.0006
	>20000	4	1750	2	**<0.59**	1:0.0011
	>20000	4	1750	3	**<0.84**	1:0.0017
	>20000	4	875	1	**<0.29**	1:0.0011
	>20000	4	875	2	**<0.54**	1:0.0023
	>20000	4	875	3	**<0.79**	1:0.0034
	>20000	4	437.5	2	**<0.52**	1:0.0046
	>20000	4	437.5	3	**<0.77**	1:0.0069
	>20000	4	218.75	3	**<0.76**	1:0.0137

A: Surf. D; B: DTEA
Media: PDB; Inoculum size: 1.156E+06

	PPM AI MIC Values (3rd day)				S.I.	Ratio (Ca: Cb)
Test	Alone		Combination			
Organism	CA	CB	Ca	Cb		
	>20000	100	20000	50	**>1.50**	1:0.0025
	>20000	100	20000	60	**>1.60**	1:0.0030
A.niger	>20000	100	20000	80	**>1.80**	1:0.0040
ATCC#16404	>20000	100	10000	40	**<0.90**	1:0.0040
	>20000	100	10000	50	**>1.00**	1:0.0050
	>20000	100	10000	60	**>1.10**	1:0.0060
	>20000	100	10000	80	**>1.30**	1:0.0080
	>20000	100	5000	30	**<0.55**	1:0.0060
	>20000	100	5000	40	**<0.65**	1:0.0080
	>20000	100	5000	50	**<0.75**	1:0.0100
	>20000	100	5000	60	**<0.85**	1:0.0120
	>20000	100	5000	80	**>1.05**	1:0.0160
	>20000	100	2500	20	**<0.33**	1:0.0080
	>20000	100	2500	30	**<0.43**	1:0.0120
	>20000	100	2500	40	**<0.53**	1:0.0160
	>20000	100	2500	50	**<0.63**	1:0.0200
	>20000	100	2500	60	**<0.73**	1:0.0240
	>20000	100	2500	80	**<0.93**	1:0.0320
	>20000	100	1750	20	**<0.29**	1:0.0114
	>20000	100	1750	40	**<0.49**	1:0.0229
	>20000	100	1750	50	**<0.59**	1:0.0286
	>20000	100	1750	60	**<0.69**	1:0.0343
	>20000	100	1750	80	**<0.89**	1:0.0457
	>20000	100	875	30	**<0.34**	1:0.0343
	>20000	100	875	40	**<0.44**	1:0.0457
	>20000	100	875	50	**<0.54**	1:0.0571
	>20000	100	875	60	**<0.64**	1:0.0686
	>20000	100	875	80	**<0.84**	1:0.0914
	>20000	100	437.5	20	**<0.22**	1:0.0457
	>20000	100	437.5	30	**<0.32**	1:0.0686
	>20000	100	437.5	40	**<0.42**	1:0.0914
	>20000	100	437.5	50	**<0.52**	1:0.1143
	>20000	100	437.5	60	**<0.62**	1:0.1371
	>20000	100	437.5	80	**<0.82**	1:0.1829
	>20000	100	218.75	40	**<0.41**	1:0.1829
	>20000	100	218.75	50	**<0.51**	1:0.2286
	>20000	100	218.75	60	**<0.61**	1:0.2743
	>20000	100	218.75	80	**<0.81**	1:0.3657

A: Surf. D
B: DTEA
Media: PDB
Inoculum size 5.72E+05

	PPM AI MIC Values (48hrs)				S.I.	Ratio (Ca: Cb)
Test	Alone		Combination			
Organism	CA	CB	Ca	Cb		
C.albicans	>20000	40	2500	30	**<0.88**	1:0.0100
ATCC#10203	>20000	40	1750	30	**<0.84**	1:0.0100
	>20000	40	875	30	**<0.79**	1:0.0100
	>20000	40	437.5	30	**<0.77**	1:0.0200
	>20000	40	218.75	30	**<0.76**	1:0.0914

A:Surf. D
B:DTEA
Media: 1/10 TSB
Inoculum size:1.16E+06

	PPM AI MIC Values (24hrs)				S.I.	Ratio (Ca: Cb)
Test	Alone		Combination			
Organism	CA	CB	Ca	Cb		
Ps.aeruginosa	>20000	20	2500	8	**<0.53**	1:0.0032
ATCC#15442	>20000	20	2500	10	**<0.63**	1:0.0040
	>20000	20	1750	10	**<0.59**	1:0.0057

A:Surf. D
B:DTEA
Media: 1/10 TSB
Inoculum size:1.8E+05

	PPM AI MIC Values (24hrs)				S.I.	Ratio (Ca: Cb)
Test	Alone		Combination			
Organism	CA	CB	Ca	Cb		
S.aureus	>20000	5	2500	4	**<0.93**	1:0.0016
ATCC# 6538	>20000	5	1750	4	**<0.89**	1:0.0023
	>20000	5	875	3	**<0.64**	1:0.0034
	>20000	5	875	4	**<0.84**	1:0.0046
	>20000	5	437.5	2	**<0.42**	1:0.0046
	>20000	5	437.5	3	**<0.62**	1:0.0069
	>20000	5	437.5	4	**<0.82**	1:0.0091
	>20000	5	218.75	3	**<0.41**	1:0.0091
	>20000	5	218.75	3	**<0.61**	1:0.0137
	>20000	5	218.75	4	**<0.81**	1:0.0183

A:Surf. E
B:DTEA
Media: 1/10 TSB
Inoculum size:8.13E+07
P. aeruginosa ATCC#15442 **No Synergy**

A:Surf. E
B:DTEA
Media: PDB
Inoculum size 1.56E+06

	PPM AI MIC Values (3rd day)				S.I.	Ratio (Ca: Cb)
Test	Alone		Combination			
Organism	CA	CB	Ca	Cb		
A.niger	>20000	200	5000	50	**<0.50**	1:0.0100
ATCC#16404	>20000	200	5000	60	**<0.55**	1:0.0120
	>20000	200	5000	80	**<0.65**	1:0.0160
	>20000	200	5000	100	**<0.75**	1:0.0200
	>20000	200	2500	30	**<0.28**	1:0.0120
	>20000	200	2500	40	**<0.33**	1:0.0160
	>20000	200	2500	50	**<0.38**	1:0.0200
	>20000	200	2500	60	**<0.43**	1:0.0240
	>20000	200	2500	80	**<0.53**	1:0.0320
	>20000	200	2500	100	**<0.63**	1:0.0400
	>20000	200	1750	30	**<0.24**	1:0.0171
	>20000	200	1750	40	**<0.29**	1:0.0229
	>20000	200	1750	50	**<0.34**	1:0.0286
	>20000	200	1750	60	**<0.39**	1:0.0343
	>20000	200	1750	80	**<0.49**	1:0.0457
	>20000	200	1750	100	**<0.59**	1:0.0571
	>20000	200	875	30	**<0.19**	1:0.0343
	>20000	200	875	40	**<0.24**	1:0.0457
	>20000	200	875	50	**<0.29**	1:0.0571
	>20000	200	875	60	**<0.34**	1:0.0686
	>20000	200	875	80	**<0.44**	1:0.0914
	>20000	200	875	100	**<0.54**	1:0.1143
	>20000	200	437.5	40	**<0.22**	1:0.0914
	>20000	200	437.5	50	**<0.27**	1:0.1143
	>20000	200	437.5	60	**<0.32**	1:0.1371
	>20000	200	437.5	80	**<0.42**	1:0.1829
	>20000	200	437.5	100	**<0.52**	1:0.2286
	>20000	200	218.75	60	**<0.31**	1:0.2743
	>20000	200	218.75	80	**<0.41**	1:0.3657
	>20000	200	218.75	100	**<0.51**	1:0.4571

A:Surf. E
B:DTEA
Media: PDB
Inoculum size 1.8E+06

	PPM AI MIC Values (48hrs)				S.I.	Ratio (Ca: Cb)
Test	Alone		Combination			
Organism	CA	CB	Ca	Cb		
	>20000	50	10000	40	**>1.30**	1:0.0040
C.albicans	>20000	50	5000	30	**<0.85**	1:0.0060
ATCC#10203	>20000	50	5000	40	**>1.05**	1:0.0080
	>20000	50	2500	20	**<0.53**	1:0.0080
	>20000	50	2500	30	**<0.73**	1:0.0120
	>20000	50	2500	40	**<0.93**	1:0.0160
	>20000	50	1750	20	**<0.49**	1:0.0114
	>20000	50	1750	30	**<0.69**	1:0.0171
	>20000	50	1750	40	**<0.89**	1:0.0229
	>20000	50	875	30	**<0.64**	1:0.0343
	>20000	50	875	40	**<0.84**	1:0.0457
	>20000	50	437.5	30	**<0.62**	1:0.0686
	>20000	50	437.5	40	**<0.82**	1:0.0914
	>20000	50	218.75	40	**<0.81**	1:0.1829

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A: Surf. E
B: DTEA
Media: 1/10 TSB
Inoculum size:1.156E+06

	PPM AI MIC Values (24hrs)				S.I.	Ratio (Ca: Cb)
Test	Alone		Combination			
Organism	CA	CB	Ca	Cb		
S.aureus	20000	5	1750	4	**<0.89**	1:0.0023
ATCC# 6538	20000	5	875	3	**<0.64**	1:0.0034
	20000	5	875	4	**<0.84**	1:0.0046
	20000	5	437.5	1	**<0.22**	1:0.0023
	20000	5	437.5	2	**<0.42**	1:0.0046
	20000	5	437.5	3	**<0.62**	1:0.0069
	20000	5	437.5	4	**<0.82**	1:0.0091
	20000	5	218.75	2	**<0.41**	1:0.0091
	20000	5	218.75	3	**<0.61**	1:0.0137
	20000	5	218.75	4	**<0.81**	1:0.0183

The following biocides had no synergy against any organism tested when paired with the following surfactants:

Surf. A

Sodium Benzoate, TRIS NITRO

Surf. E

DMDMH

Surf. D

CS-1246, OPP, DMDMH

In the following combinations, the ratio of surfactant to biocide where synergy was observed were not commercially relevant, i.e., a ratio of 1:0.2 or greater (less biocide relative to surfactant). At these ratios, the biocide levels in a formulated product would be too low to be practical:

Surf. A

DIDAC, IPBC

Surf. E

CMIT/MIT, IPBC, OIT, TTPC, WSCP

Surf. D

CMIT/MIT, OIT, DIDAC

(MBIT, IPBC, WSCP were synergistic only at 1:0.05 or worse except for one data point)

CLAIMS

1. A synergistic microbicidal composition comprising: (a) a nonionic surfactant with structure:

$$R^1O(CH_2CH(CH_3)O)_5(CH_2CH_2O)_9H$$

where R^1 is a C_8 alkyl group; and (b) 2-decylthioethylamine; wherein a weight ratio of said nonionic surfactant to 2-decylthioethylamine is from 1:0.004 to 1:0.0137 or 1:0.016 to 1:0.4571.

2. The synergistic microbicidal composition of claim 1 in which R^1 is 2-ethylhexyl.

3. A method for inhibiting the growth of microorganisms in an aqueous medium; said method comprising adding to said aqueous medium: (a) a nonionic surfactant with structure:

$$R^1O(CH_2CH(CH_3)O)_5(CH_2CH_2O)_9H$$

where R^1 is a C_8 alkyl group; and (b) 2-decylthioethylamine; wherein a weight ratio of said nonionic surfactant to 2-decylthioethylamine is from 1:0.004 to 1:0.0137 or 1:0.016 to 1:0.4571.

4. The method of claim 3 in which R^1 is 2-ethylhexyl..

5. A synergistic microbicidal composition comprising: (a) a nonionic surfactant with structure:

$$R^2O(CH_2CH(CH_3)O)_3(CH_2CH_2O)_7H$$

where R^2 is a mixture of C_8-C_{14} linear alkyl groups; and (b) 2-decylthioethylamine; wherein a weight ratio of said nonionic surfactant to 2-decylthioethylamine is from 1:0.0023 to 1:0.4571.

6. The synergistic microbicidal composition of claim 5 in which said mixture of C_8-C_{14} linear alkyl groups comprises from 60 to 75 wt% C_8-C_{10} linear alkyl groups and 25 to 40 wt% C_{12}-C_{14} linear alkyl groups..

7. A method for inhibiting the growth of microorganisms in an aqueous medium; said method comprising adding to said aqueous medium: (a) a nonionic surfactant with structure:

$$R^2O(CH_2CH(CH_3)O)_3(CH_2CH_2O)_7H$$

where R^2 is a mixture of C_8-C_{14} linear alkyl groups; and (b) 2-decylthioethylamine; wherein a weight ratio of said nonionic surfactant to 2-decylthioethylamine is from 1:0.0023 to 1:0.4571.

8. The method of claim 7 in which said mixture of C_8-C_{14} linear alkyl groups comprises from 60 to 75 wt% C_8-C_{10} linear alkyl groups and 25 to 40 wt% C_{12}-C_{14} linear alkyl groups.

9. A synergistic microbicidal composition comprising: (a) a nonionic surfactant with structure:

$$R^2O(CH_2CH(CH_3)O)_3(CH_2CH_2O)_5H$$

where R^2 is a mixture of C_8-C_{14} linear alkyl groups; and (b) 2-decylthioethylamine; wherein a weight ratio of said nonionic surfactant to 2-decylthioethylamine is from 1:0.0023 to 1:0.3657.

10. The synergistic microbicidal composition of claim 9 in which said mixture of C_8-C_{14} linear alkyl groups comprises from 60 to 75 wt% C_8-C_{10} linear alkyl groups and 25 to 40 wt% C_{12}-C_{14} linear alkyl groups.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/058951

A. CLASSIFICATION OF SUBJECT MATTER
INV. A01N33/08 A01N25/30 A01P1/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 266 828 A1 (DOW CHEMICAL CO [US]) 11 May 1988 (1988-05-11) examples 3-8 page 4, line 14 - line 16 -----	1-10
A	US H 1265 H (BRADY BONNIE M F [US] ET AL) 7 December 1993 (1993-12-07) examples C-238 - C-240 table II -----	1-10
A	STEPHANIE S. ADKINS ET AL: "Morphology and Stability of CO2-in-Water Foams with Nonionic Hydrocarbon Surfactants", LANGMUIR, vol. 26, no. 8, 20 April 2010 (2010-04-20), pages 5335-5348, XP055115328, ISSN: 0743-7463, DOI: 10.1021/la903663v the whole document -----	1-10
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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

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"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 when the document is taken alone

"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

Date of the actual completion of the international search	Date of mailing of the international search report
10 December 2014	18/12/2014

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/058951

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2008/088647 A1 (DOW GLOBAL TECHNOLOGIES INC [US]; VARINEAU PIERRE T [US]; WEBER KARA S) 24 July 2008 (2008-07-24) the whole document -----	1-10
A	WO 2009/155187 A1 (DOW GLOBAL TECHNOLOGIES INC [US]; VARINEAU PIERRE T [US]; BUSBY MOLLY) 23 December 2009 (2009-12-23) examples 2, 8 table 10 -----	1-10

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2014/058951

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0266828 A1	11-05-1988	AU 613587 B2	08-08-1991
		AU 7998387 A	28-04-1988
		BR 8705619 A	31-05-1988
		CA 1326919 C	08-02-1994
		DE 3778296 D1	21-05-1992
		DK 554387 A	23-04-1988
		EP 0266828 A1	11-05-1988
		ES 2030712 T3	16-11-1992
		JP 2573627 B2	22-01-1997
		JP S63146801 A	18-06-1988
		NO 874392 A	25-04-1988
US H1265 H	07-12-1993	NONE	
WO 2008088647 A1	24-07-2008	AR 064847 A1	29-04-2009
		BR PI0720328 A2	24-12-2013
		CN 101578130 A	11-11-2009
		EP 2117693 A1	18-11-2009
		JP 5346299 B2	20-11-2013
		JP 2010515805 A	13-05-2010
		TW 200843843 A	16-11-2008
		US 2010081607 A1	01-04-2010
		WO 2008088647 A1	24-07-2008
WO 2009155187 A1	23-12-2009	AU 2009260327 A1	23-12-2009
		CA 2728411 A1	23-12-2009
		CN 102066540 A	18-05-2011
		EP 2310481 A1	20-04-2011
		JP 2011524940 A	08-09-2011
		US 2011098492 A1	28-04-2011
		WO 2009155187 A1	23-12-2009