

AQUEOUS ANTI-MICROBIAL COMPOSITIONS CONTAINING ORGANOTIN COMPOUNDS

5 Background of the Invention

This invention relates to anti-microbial compositions containing organotin compounds.

Organotin compounds (and, in particular, trialkyl tin compounds such as tributyl tin oxide) have been used as anti-microbial agents in compositions for protecting materials such as wood against the growth of microorganisms such as fungi. Because most of these organotin compounds have limited solubility in water, they remain on the treated surface following application despite exposure to rain or snow.

15 As a consequence of the limited water solubility of the organotin compounds, these compositions have been primarily organic solvent-based. From the standpoint of environmental safety, however, it would be desirable to provide the organotin compounds in the form of aqueous-based compositions.

20 **Summary of the Invention**

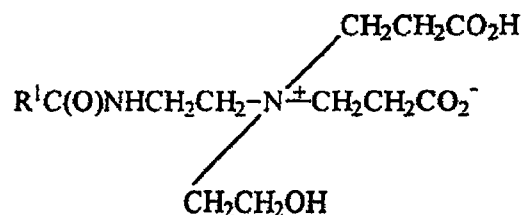
In general, the invention features a stable, aqueous, anti-microbial composition that includes one or more organotin compounds and one or more surfactants for solubilizing the organotin compounds in water. The surfactants are selected from the group consisting essentially of:

25 (i) surfactants comprising a non-ionic ethylene oxide-propylene oxide
block copolymer having the formula



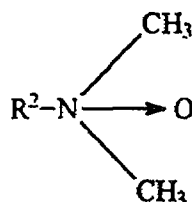
30 where x ranges from about 1-30 and y ranges from about 1-30;

(ii) surfactants comprising an amine-acid having the formula



where R^1 is a branched or straight chain C_{10} - C_{18} alkyl group;

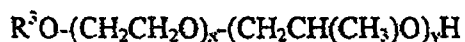
(iii) surfactants comprising an amine-oxide having the formula



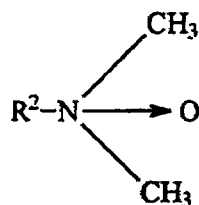
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where R^2 is a branched or straight chain C_{10} - C_{18} alkyl group; and combinations thereof.

In one preferred embodiment, the surfactant includes a non-ionic
 10 ethylene oxide-propylene oxide block copolymer surfactant having the formula

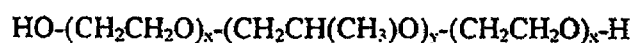


where R^3 is a straight chain or branched C_{12} - C_{14} alkyl group, x ranges from about
 15 1-30, and y ranges from about 1-30. Particularly preferred are block copolymers according to this formula where x is 4 and y is 4. Also preferred are mixtures of surfactants where copolymers according to this formula are combined with an amine-oxide having the formula



where R^2 is a branched or straight chain C_{10} - C_{18} alkyl group.

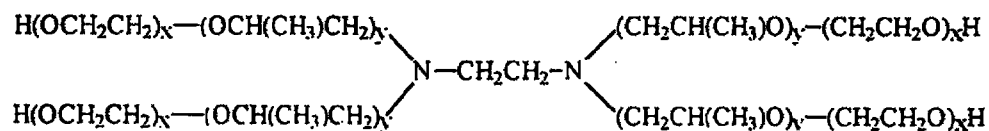
In another preferred embodiment, the surfactant includes a non-ionic
5 ethylene oxide-propylene oxide block copolymer surfactant having the formula



where x ranges from about 1-30 and y ranges from about 1-30.

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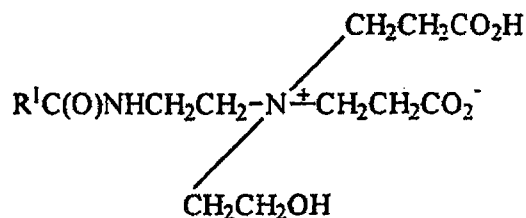
In a third preferred embodiment, the surfactant includes a non-ionic
ethylene oxide-propylene oxide block copolymer surfactant having the formula



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where x ranges from about 1-30 and y ranges from about 1-30.

In a fourth preferred embodiment, the surfactant includes an amine-acid
having the formula

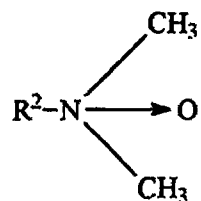


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where R^1 is a branched or straight chain $C_{10} - C_{18}$ alkyl group.

In a fifth preferred embodiment, the surfactant includes an amine-oxide having the formula

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where R^2 is a lauryl group.

10 The organotin compound preferably includes a trialkyl tin compound, e.g., tributyl tin oxide. The weight to weight ratio of the organotin compound to the surfactant ranges from about 1:0.5 to 1:20, and more preferably from about 1:1 to 1:6. To further enhance anti-microbial ability, the composition may also include zinc or a complex thereof.

15 The composition may further include one or more water-miscible organic co-solvents in an amount no greater than about 25% by weight to help solubilize the organotin compound in water. Even more preferred, however, are compositions that are essentially free of organic co-solvents. The composition preferably is optically clear.

20 As used throughout this application:

A "stable" composition is a composition that does not exhibit macroscopic phase separation (i.e., does not separate upon standing into two distinct layers), as determined by visual inspection, after time periods up to 36 hours at 25°C.

25 An "optically clear" composition is a composition that appears substantially as clear as distilled water upon visual inspection at 25°C.

A "water-miscible organic co-solvent" is an organic solvent that is miscible in water at 25°C.

The invention provides anti-microbial compositions that are water-based, thereby minimizing the hazards associated with solvent-based organotin anti-microbial formulations. The compositions are also relatively easy to manufacture and apply to any of a variety of water-safe surfaces (e.g., by spraying). Furthermore, the compositions exhibit potent anti-microbial activity.

Other features and advantages of the invention will be apparent from the following description of the preferred embodiments thereof, and from the claims.

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Description of the Preferred Embodiments

The invention features stable, aqueous, anti-microbial compositions in which one or more organotin compounds are combined with one or more surfactants chosen from the three general classes set forth in the Summary of the Invention, above. The purpose of the surfactants is to help solubilize the normally water-insoluble (or sparingly water-soluble) organotin compounds in the aqueous medium. The physical appearance of the compositions ranges from optically clear solutions to turbid, milky-white emulsions, with the optically clear solutions being preferred. Regardless of the physical appearance, however, the compositions are stable (i.e., they do not separate upon standing into two distinct layers, as determined by visual inspection, after time periods up to 36 hours at 25°C).

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As set forth in the Summary of the Invention, the first class of surfactants includes non-ionic ethylene oxide-propylene oxide block copolymer having the formula

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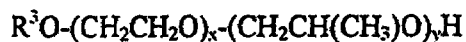


where x ranges from about 1-30 and y ranges from about 1-30. Examples of suitable surfactants falling within this class are commercially available and include ethylene oxide-propylene oxide block copolymers available from Union Carbide Chemicals and Plastics Co. Inc. of Danbury, CT under the trade designations

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"Tergitol MIN-Foam 1X Surfactant" and "Tergitol MIN-Foam 2X Surfactant."

These surfactants are water-miscible, polyalkylene glycol ethers having the formula



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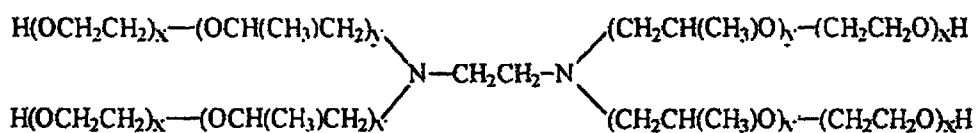
where R^3 is a straight chain or branched $C_{12} - C_{14}$ alkyl group, x is 4, and y is 4.

The Tergitol MIN-Foam 1X Surfactant has a molecular weight of 640, a specific gravity of 0.995 at 20°C, and a freezing point of -42°C, whereas the Tergitol MIN-Foam 2X Surfactant has a molecular weight of 647, a specific gravity of 0.978 at 20°C, and a freezing point of -47°C.

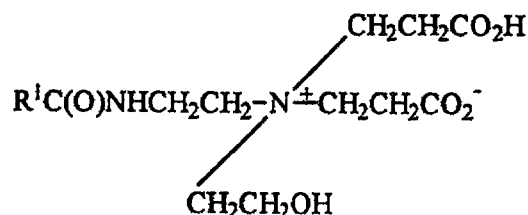
Other commercially available surfactants falling into the first general class include those sold by BASF Corp. of Parsippany, NJ under the trade designations "Pluronic" and "Tetronic" block copolymer surfactants. The Pluronic surfactants have the general formula



where x ranges from about 1-30 and y ranges from about 1-30. The Tetronic surfactants have the general formula

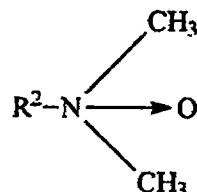


where x ranges from about 1-30 and y ranges from about 1-30. The second general class of suitable surfactants includes amine-acids having the general formula



where R^1 is a branched or straight chain $\text{C}_{10} - \text{C}_{18}$ alkyl group. Examples of suitable surfactants falling within this general class are commercially available and include those sold by Rhone-Poulenc of Cranbury, NJ under the trade designation "Miranol C2M AA," (a cocoamphodipropionic acid).

The third general class of suitable surfactants includes amine-oxides having the general formula



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where R^2 is a branched or straight chain $\text{C}_{10} - \text{C}_{18}$ alkyl group. Examples of suitable surfactants falling within this general class are commercially available and include those sold by Rhone-Poulenc of Cranbury, NJ under the trade designation "Rhodamox LO," an amine-oxide surfactant in which R^2 is a lauryl group.

The organotin compound preferably is a trialkyl tin compound exhibiting anti-microbial activity. Such compounds are well-known in the art. Particularly preferred are tributyl tin compounds. Examples include tributyl tin oxide, tributyl tin phosphate, tributyl tin benzoate, tributyl tin borate, tributyl tin carbonate, tributyl tin nitrate, tributyl tin ethane sulfonate, tributyl tin sulfide, tributyl tin chloride, tributyl tin naphthenate, the reaction product of tributyl tin oxide and a long-chain

carboxylic acid (e.g., tributyl tin linoleate), and combinations thereof. The most preferred organotin compound is tributyl tin oxide.

The relative amounts of organotin compound and surfactant are chosen such that the organotin compound is solubilized in the aqueous medium (e.g., in the form of an optically clear solution or a turbid, milky-white emulsion) using a minimum amount of surfactant. In general, the weight to weight ratio of the total amount of organotin compound(s) to the total amount of surfactant(s) ranges from about 1:0.5 to 1:20, and preferably from about 1:1 to 1:6.

Preferably, the surfactant is used alone, without a water-miscible, organic co-solvent. For example, Tergitol MIN-Foam 2X, when combined with tributyl tin oxide in a weight to weight ratio of 1 part tributyl tin oxide to 2 parts surfactant at a pH of 6.0-7.0, yields a stable, optically clear solution. With other surfactants, however, it may be necessary to add one or more water-miscible, organic co-solvents in order to solubilize the organotin compound. The amount of co-solvent generally used is the minimum amount necessary to achieve a stable solution, with the maximum amount of co-solvent being no greater than about 25% by weight.

Suitable co-solvents generally fall into two classes. The first class includes co-solvents having an infinite solubility in water at 25°C. Examples include oxygenated solvents such as lower alkyl alcohols (e.g., methanol, ethanol, and isopropanol). When incorporated into an aqueous organotin-containing composition, the stability of the composition increases as the weight percentage of the co-solvent increases, up to a maximum of about 25% by weight.

The second class includes co-solvents having limited solubility in water at 25°C. Examples include higher alkyl alcohols such as butanol and pentanol. With these solvents, the stability of the composition increases as the amount of co-solvent reaches its solubility limit (e.g., 7.7 g/100 g water in the case of butanol and 2.7 g/100 g water in the case of pentanol).

The pH of the composition is also chosen to maximize the stability of the composition. As those of ordinary skill in the art will readily appreciate, the selection of any particular pH value depends upon the specific combination of organotin compound and surfactant being employed.

5 The compositions may be used to remove existing fungal growth or to inhibit such growth altogether. They may be applied to substrates such as wood and masonry surfaces by a variety of means, including brushing, padding, rolling, and spraying, with spraying being preferred. In addition, the compositions may be incorporated into a water-based paint or varnish.

10 The invention will now be further described by way of the following examples.

EXAMPLES

Example 1

15 An anti-microbial composition was prepared by combining 2 g of tributyl tin oxide (commercially available from ATOchem North America, Inc. of Philadelphia PA) and 4 g of Tergitol MIN-Foam 2X Surfactant (commercially available from Union Carbide of Danbury, CT) at room temperature, followed by dilution with 94 g of deionized water. The pH was then adjusted to 6.0-7.0 through
20 addition of 1N HCl to yield an optically clear solution.

Example 2

 The procedure of Example 1 was followed except that 1 g of tributyl tin oxide was combined with 2 g of Tergitol MIN-Foam 2X Surfactant, followed by dilution with 97 g of deionized water. After adjusting the pH to 6.0-7.0 through
25 addition of 1N HCl, an optically clear solution resulted.

Example 3

The procedure of Example 1 was followed except that 1 g of tributyl tin oxide was combined with 4 g of Miranol C2M AA surfactant (commercially available from Rhone-Poulenc of Cranbury, NJ), followed by dilution with 95 g of deionized water. The resulting composition was in the form of a milky-white emulsion having a pH of 9.4. The emulsion was stable up to one week.

Example 4

The procedure of Example 1 was followed except that 1 g of tributyl tin oxide was combined with 4 g of Rhodamox LO surfactant (commercially available from Rhone-Poulenc of Cranbury, NJ), followed by dilution with 95 g of deionized water. The resulting composition was in the form of an optically clear solution having a pH of 8.1.

Example 5

The procedure of Example 1 was followed except that 1 g of tributyl tin oxide was combined with 2 g of Tergitol MIN-Foam 1X Surfactant (commercially available from Union Carbide of Danbury, CT), followed by 10 g of a co-solvent mixture containing 6 g of 1-propanol and 4 g of 1-butanol. The resulting solution was diluted with 87 g of deionized water, followed by addition of 1N HCl to bring the pH of the solution to 6.4. The resulting solution was optically clear.

Example 6

The procedure of Example 1 was followed except that 1 g of tributyl tin oxide was combined with 2 g of Pluronic P 62 Surfactant (commercially available from BASF of Parsippany, NJ), followed by 10 g of a co-solvent mixture containing 5 g of 1-propanol and 5 g of 1-butanol. The resulting solution was diluted with 87 g of deionized water, followed by addition of 1N HCl to bring the pH of the solution to 7.8. The resulting solution was optically clear.

Example 7

The procedure of Example 1 was followed except that 1 g of tributyl tin oxide was combined with 2 g of Tetronic 304 Surfactant (commercially available from BASF of Parsippany, NJ), followed by 15 g of a co-solvent mixture containing 10 g of 1-propanol and 5 g of 1-butanol. The resulting solution was diluted with 82

g of deionized water, followed by addition of 1N HCl to bring the pH of the solution to 6.5. The resulting solution was translucent.

Example 8

The procedure of Example 3 was followed except the amount of surfactant was 5 g and the amount of deionized water was 65.5 g. After combining the surfactant and the tributyl tin oxide, 28.5 g of a zinc complex was added. The zinc complex, which formed zinc oxide (a mild anti-fungicide) upon drying, was prepared by combining 4.5 g of ethylenediamine tetraacetic acid (Aldrich Chemical Co., Milwaukee, WI), 7.0 g of triethylamine (Aldrich Chemical Co., Milwaukee, WI), 2.0 g of zinc chloride (Aldrich Chemical Co., Milwaukee, WI), and 15.0 g of deionized water. The resulting composition was in the form of an optically clear solution having a pH of 12.9.

Example 9

The procedure of Example 8 was followed except that the surfactant was Rhodamox LO (5 g). The composition was in the form of an optically clear solution.

Example 10

The anti-microbial efficacy of compositions according to the invention was performed according to test methods set forth in ASTM-G21-90, which is designed to determine the effect of fungi on the properties of different materials. The test procedure involves (1) selection of suitable specimens for determination of pertinent properties, (2) inoculation of the specimens with suitable organisms, (3) exposure of inoculated specimens to conditions favorable to growth, and (4) examination of the inoculated specimens and rating for visual growth.

Here, two substrates (virgin birch panel and granule shingle), were each cut into squares measuring 2 in. (5.08 cm) by 2 in. (5.08 cm). Each square (with the exception of the control) was then treated with one of the following anti-microbial compositions of the invention:

- Composition B: The anti-microbial composition of Example 1;
- Composition C: The anti-microbial composition of Example 8;
- Composition D: The anti-microbial composition of Example 9.

In addition, squares were treated with the following compositions for the sake of comparison:

Comparative Composition A: A solvent-based composition containing tributyl tin oxide (2% by weight) in methanol;

5 Comparative Composition E: A petroleum distillate-based composition commercially available from PPG Architectural Paint of Pittsburgh, PA under the designation "Olympic Clearwood Preservative" containing, as the active ingredients, tributyl tin oxide and Folpet[N-(trichloromethylthio) phthalimide];

10 Comparative Composition F: A petroleum distillate-based composition commercially available from DAP Inc. of Dayton, OH under the designation "DAP Wood Life Wood Preservative" containing, as the active ingredient, 3-iodo-2-propynyl butyl carbamate.

The compositions were applied by brush. In addition, two panels were left untreated for use as control samples.

15 Following treatment, the samples were placed on a minimal salts agar plate and sprayed with a fungal spore suspension of known concentration containing the following five organisms: *Aspergillus niger* (ATCC 9642), *Penicillium prinophilum* (ATCC 11797), *Chaetomium globosum* (ATCC 6205), *Gliocladium virens* (ATCC 9645), and *Aureobasidium pullulans* (ATCC 15233).

20 The concentration of each microorganism was 10^6 /50 ml. Following microorganism inoculation, the samples were incubated at 28°C/95% relative humidity for a total of 28 days. Visual inspections were made every 7 days. The rating standard is defined as follows:

0: No fungal growth observed.

25 1: Trace growth, 1 to 10% coverage of sample surface by molds.

2: Light growth, 10-30% coverage of sample surface by molds.

3: Moderate growth, 30 to 60% coverage of sample surface by molds.

4: Heavy growth, more than 60% coverage of sample surface by molds.

The results are shown in Table I.

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TABLE I

Composition	Sample	Growth Rating			
		Day 7	Day 14	Day 21	Day 28
Control	Shingle	1	1	2	3
	Wood	3	3	4	4
A	Shingle	0	0	0.1*	0.1*
	Wood	0	1	1	3
B	Shingle	0	0	0	0
	Wood	0	0	0	1
C	Shingle	0	0	0	0
	Wood	0	0	0	0
D	Shingle	0	0	0	0
	Wood	0	0	0	0
E	Shingle	2	2	2	3
	Wood	1	1	2	2
F	Shingle	0	1	2	4
	Wood	0	0	0	0

* Growth apparent only along cut edges of sample.

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Example 11

An aqueous anti-microbial solution containing 1% by weight tributyl tin oxide and 2% by weight Tergitol MIN-Foam 2X Surfactant was brushed on the wood shingles of lake front cabin located in Hayward, WI, and on a wood patio bench situated on the cabin site. Both the shingles and the bench were covered with heavy green algae. After 25 days, the treated areas were completely discolored, indicating algae removal, and maintained the same freshness 14 months after application.

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The roof of the cabin was made of granule shingles approximately 20 years old, and was covered with heavy green algae, white and gray molds, and thick

lichens. Without any pre-conditioning, two sections of the roof were sprayed evenly with the above-described anti-microbial composition by means of an air-pump garden spray at a rate of about 120 square feet per gallon (42.2 square meters per liter). Within six weeks, heavy molds were killed, delaminated from the roof, and finally cleaned away by rain and wind, thereby restoring the treated area to its original color. There was a clear boundary between the treated area and the untreated area. No rundown or leachout pattern was observed.

Example 12

A concentrate was formed by combining the following:

10	Tributyl tin oxide	16.0 g
	Tergitol MIN-Foam 2X	8.0 g
	Rhodamox LO (30% solids)	48.0 g
	Deionized water	28.0 g

The resulting solution was clear and had a pH of 7.51. It had a specific gravity of 1.011 and a cloud point of greater than 68°C (the cloud point is the temperature at which the solute begins to separate from the solution). The concentrate can be diluted to any desired concentration through addition of water.

The concentrate may also be prepared using tap water instead of deionized water for reasons of economy and convenience. Because tap water often contains metal ions such as calcium, magnesium, and fluoride ions, it may be necessary to incorporate one or more chelating agents in the composition to prevent these ions from inducing instability or precipitation. Suitable chelating agents for this purpose are well-known and include, for example, ethylene diamine tetraacetic acid (EDTA), nitrilotriacetic acid (NTA), citric acid, and gluconic acid, as well as salts thereof. The particular amount of chelating agent needed depends upon the ion content of the water. In general, however, the amount ranges from about 0.1 to 3.0% by weight.

Other embodiments are within the following claims.

What is claimed is:

1. A stable, aqueous, anti-microbial composition comprising:

(a) one or more organotin compounds; and

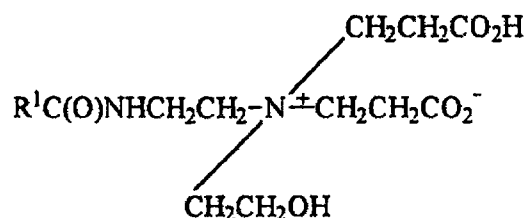
5 (b) one or more surfactants for solubilizing said organotin compounds in water selected from the group consisting essentially of:

(i) surfactants comprising a non-ionic ethylene oxide-propylene oxide block copolymer having the formula



where x ranges from about 1-30 and y ranges from about 1-30;

(ii) surfactants comprising an amine-acid having the formula

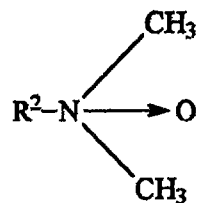


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where R^1 is a branched or straight chain $\text{C}_{10} - \text{C}_{18}$ alkyl group;



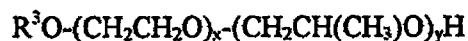
(iii) surfactants comprising an amine-oxide having the formula



5 where R^2 is a branched or straight chain C_{10} - C_{18} alkyl group;
and combinations thereof.

2. A composition according to claim 1 comprising a non-ionic ethylene
oxide-propylene oxide block copolymer surfactant having the formula

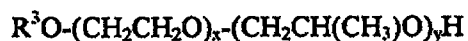
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where R^3 is a straight chain or branched C_{12} - C_{14} alkyl group, x ranges from about
1-30, and y ranges from about 1-30.

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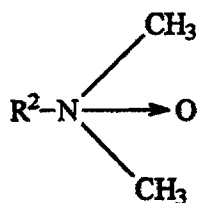
3. A composition according to claim 1 comprising a non-ionic ethylene
oxide-propylene oxide block copolymer surfactant having the formula



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where R^3 is a straight chain or branched C_{12} - C_{14} alkyl group, x ranges from about
1-30, and y ranges from about 1-30, and an amine oxide having the formula

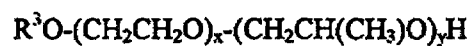




where R^2 is a branched or straight chain C_{10} - C_{18} alkyl group.

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4. A composition according to claim 1 comprising a non-ionic ethylene oxide-propylene oxide block copolymer surfactant having the formula

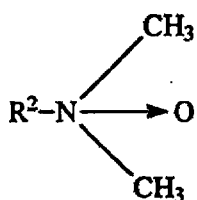


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where R^3 is a straight chain or branched C_{12} - C_{14} alkyl group, x is 4, and y is 4.

5. A composition according to claim 1 comprising an amine-oxide surfactant having the formula

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where R^2 is a lauryl group.

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6. A composition according to claim 1 comprising tributyl tin oxide.



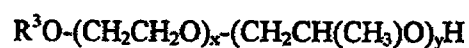
7. A composition according to claim 1 wherein said composition is essentially free of organic co-solvents.

8. A composition according to claim 1 wherein the weight to weight
5 ratio of said organotin compound to said surfactant ranges from about 1:0.5 to 1:20.

9. A stable, aqueous, anti-microbial composition comprising:

(a) one or more organotin compounds; and

10 (b) a surfactant for solubilizing said organotin compounds comprising a non-ionic ethylene oxide-propylene oxide block copolymer having the formula



15 where R^3 is a straight chain or branched $C_{12} - C_{14}$ alkyl group, x ranges from about 1-30, and y ranges from about 1-30.

10. A composition according to claim 9 comprising tributyl tin oxide.

20 11. A composition according to claim 9 wherein the weight to weight ratio of said organotin compound to said surfactant ranges from about 1:0.5 to 1:20.

