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## ORGANO BISMUTH BIOCIDES

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This invention relates to methods of preventing and/or inhibiting the growth of microorganisms, including bacteria and fungi and to compositions of matter utilized in these methods. The invention more particularly relates to materials which have been made resistant to attack by bacteria by the aforesaid methods.

It is an object of this invention to provide methods for inhibiting and/or preventing the growth of bacteria. It is also an object of this invention to provide methods for inhibiting and/or preventing the growth of fungi. It is another object of this invention to provide compositions which are useful in the aforesaid methods as the source of the active bactericidal and/or fungicidal compound(s). It is another object of this invention to provide bacteria and/or fungi resistant paints. It is another object of this invention to provide bacteria and/or fungi resistant plastics and fibrous products such as textiles and paper products. It is also an object of this invention to provide sanitizer compositions having particular utility in hospital treatment.

The method of this invention for protecting a medium susceptible to attack by microorganisms comprises applying to the locus to be protected, an active amount of at least one bismuth compound having the formula  $R'_3BiX_2$  or  $R_nBiX_{3-n}$ , wherein  $n$  is 1 or 2,  $R'$  is an aryl group, and  $R$  is an alkyl, cycloalkyl, alkenyl, or aryl group, and  $X$  is a largely ionic bonded atom or group, and is preferably halogen, oxygen, sulfur, carboxylate, phenoxide, alkoxide, mercaptide, or cyanide. The bismuth compounds showing particularly the unusual activity against bacteria are those having 1 or 2 atoms, or groups, joined to the bismuth atom by bonds having ionic characteristics.  $X$  may act as a bridging group or atom to provide bis bismuth compounds which may be classified as substituted mono bismuth compounds and are within the scope of the present invention as defined herein. Various  $R$  and  $X$  groups may be cyclized or otherwise joined. The amount of the bismuth compound effective in a given application is dependent upon a number of factors which include the substrate to be protected, the method of application, the degree of protection desired, the bismuth compound utilized, the environment, etc. The bismuth compounds have proven to be effective against a wide spectrum of bacteria including Gram negative and Gram positive bacteria. They are particularly effective against Gram negative bacteria. Certain of these compounds may be particularly characterized by their effectivity against fungi.

Of the pentavalent organo bismuth compounds useful in this invention, those in which  $R'$  is a monocyclic aryl, as exemplified by phenyl, mono- and polychlorophenyls, tolyl, lower alkoxyphenyls and xylyl, are preferred. Of the mono- and diorganic trivalent bismuth compounds those in which  $R$  is a monocyclic aryl are also preferred. Of these compounds in which the  $R$  group is an alkyl, those having less than 19 carbon atoms in the chain, and particularly those having from 3 to 8 carbon atoms are of most interest. These bismuth compounds in which  $X$  is a halogen or a carboxylate are preferred. The preferred compounds include: triphenylbismuth dihydroxide, triphenylbismuth dichloride, triphenylbismuth diacetate, triphenylbismuth disalicylate, diphenylbismuth chloride, di-

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phenylbismuth acetate, diphenylbismuth salicylate, phenylbismuth dichloride, phenylbismuth diacetate, phenylbismuth disalicylate, diphenylbismuth laurylmercaptide, triphenylbismuth dibenzoate, phenylbismuth oxide, dibutylbismuth chloride, dioctylbismuth o-phenylphenate.

It is a particular feature of the invention that unexpectedly superior inhibiting properties may be obtained by the use of compounds  $RBiX_2$  wherein  $R$  may be an alkyl, preferably a lower alkyl containing from 3 to 8 carbon atoms, and  $X$  may be selected from the group consisting of halogen, oxygen, sulfur, carboxylate, phenoxide, alkoxide, mercaptide, and cyanide. Preferred  $X$  groups may be halogen, preferably chlorine. Preferably the  $X$  groups may be the same.

Typical of the compounds which may preferably be employed in practice of this invention may be

Methylbismuth dichloride  
Methylbismuth dibromide  
Methylbismuth diacetate  
Methylbismuth oxide  
Methylbismuth sulfide  
Ethylbismuth dichloride  
Ethylbismuth dibromide  
Ethylbismuth diacetate  
Ethylbismuth oxide  
Ethylbismuth sulfide  
Propylbismuth dichloride  
Propylbismuth dibromide  
Propylbismuth diacetate  
Propylbismuth oxide  
Propylbismuth sulfide  
Propylbismuth diphenoxide  
Propylbismuth dimethoxide  
Butylbismuth dichloride  
Butylbismuth dibromide  
Butylbismuth diacetate  
Butylbismuth sulfide  
Butylbismuth diphenoxide  
Butylbismuth dimethoxide  
Butylbismuth dicyanide  
Butylbismuth dilaurylmercaptide  
Isobutylbismuth dichloride  
Isobutylbismuth dibromide  
Isobutylbismuth diacetate  
Isobutylbismuth oxide  
Isobutylbismuth sulfide  
Isobutylbismuth diphenoxide  
Isobutylbismuth dimethoxide  
Isobutylbismuth dicyanide  
Isobutylbismuth diphenylmercaptide  
n-Amylbismuth dichloride  
n-Amylbismuth dibromide  
n-Amylbismuth diacetate  
n-Amylbismuth oxide  
n-Amylbismuth sulfide  
n-Octylbismuth dichloride  
n-Octylbismuth dibromide  
n-Octylbismuth diacetate  
n-Octylbismuth oxide  
n-Octylbismuth sulfide  
2-ethylhexylbismuth dichloride  
2-ethylhexylbismuth diacetate.

It is a particular feature of this invention that those compounds  $RBiX_2$  wherein  $R$  may be butyl are particularly effective. The preferred compound may be butylbismuth dichloride.

It is a feature of this invention that germicidal activity of the hereinbefore noted compositions may be enhanced even further when the bismuth compound is used in combination with substituted ammonium compounds

$$R''_6NH_4^+A^-$$

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wherein R'' may be a hydrocarbon radical, typically alkyl, alkenyl, aryl, alkaryl, aralkyl, cycloalkyl, etc. R'' may be for example, methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, t-butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, oleyl i.e. 7-heptadecenyl, etc. phenyl, o-, m-, or p-tolyl, naphthyl, cyclohexyl, benzyl, etc.; c may be an integer, 1-4; d may be an integer, 0-3; and the sum of c and d is 4. All of the R'' groups need not be the same. It will be apparent that R'' may include a cyclic linkage in which more than one carbon atom may be joined to the nitrogen atom, e.g., a polymethylene linkage, in which case the grouping including the nitrogen atom may be the piperidino groups. Similarly, the pyridyl or the quinolyl group may be present, etc. A may be an anion of a complex-forming compound, i.e., a compound which forms a substituted ammonium complex with an amine, as is well known, typically a halide, e.g., chloride, sulfate, sulfonate, acetate, etc.

The preferred compounds which may be employed include compounds of the formula  $R''_cNH_d \cdot A$  wherein c is 4 and d is 0. The formula of these preferred quaternary ammonium compounds may be  $R''_4N \cdot A$ . Typical of these preferred quaternary ammonium compounds which may be employed may be those formed by reacting tertiary amines typified by dimethyl dodecylamine, diethyl dodecylamine, dimethyl decylamine, dimethyl octylamine, trimethyl amine, tributyl amine, triethyl amine, pyridine, etc. with halides, typified by alkyl halides such as methyl bromide, ethyl chloride, propyl bromide, methyl iodide, butyl bromide, butyl chloride, amyl iodide, benzyl chloride, etc.

The preferred quaternary ammonium compound which may be employed is an alkyl (e.g., lauryl) dimethyl benzyl ammonium chloride, typically that available under the trademark BTC824 of Onyx Chemical Co. Other specific illustrative compounds which may be employed may include (dodecylbenzyl)pyridinium chloride; lauryl dimethyl benzyl ammonium chloride; decyl dimethyl benzyl ammonium chloride; etc.

The methods of this invention may be carried out by applying the bismuth compounds (alone or preferably with the quaternary ammonium compounds) to the surface of the material to be protected and/or admixing the bismuth compounds with the material to be protected during the fabrication of said material. The bismuth compounds may be used per se, particularly when they are incorporated into the material during preparation or fabrication. Many materials, and particularly fibrous products such as textiles, may be treated by applying the bismuth compound to the surface by dipping, padding, spraying, etc. They may be used in the form of a bactericidal and/or fungicidal composition in which the bismuth compound is the active component or one of the active components. Typically the bismuth compound may be present in amount of 0.1%-10% by weight of total mixture of carrier and bismuth compound. Liquid compositions may be utilized in which the bismuth compound is dissolved and/or suspended in a solvent. Solid compositions may be utilized in which the bismuth compound is mixed with a carrier (or diluent). The carrier may be inert, such as talcs, clays, diatomaceous earth, flours, etc., or it may have activity such as that shown by the quaternary ammonium compounds. The liquid formulations of the emulsion type will often include a dispersion agent such as the anionic, cationic or nonionic surface active agents. To obtain fungicidal and/or bactericidal compositions having an extremely broad spectrum of activity, the bismuth compounds may be formulated with other active materials such as the triorganotin, pentachlorophenol, phenyl mercuric oleate, copper-8-quinolinolate, bisphenols, o-phenylphenol, polybrominated salicylanilides, and metal (zinc) dialkyl dithiocarbamates. Illustrative of the compositions useful for carrying the active bismuth compound are Examples 1-4.

#### Example 1.—Aerosol composition

	Parts by weight
Tributyltin oxide	0.02
Triphenylbismuth dichloride	0.02
5 Toluene	15.00
Fluorohydrocarbon gaseous propellant	84.96

#### Example 2.—Liquid composition

Phenylbismuth disalicylate	1
10 Water	8
Acetone	2
Lauryl dimethylbenzylammonium chloride (50%—in water)	10
Trisodium salt of N-hydroxyethylethylenediamine triacetic acid	0.4
15 Toluene	3

#### Example 3.—Emulsion composition

Tripropyltin acetate	0.02
20 Diphenylbismuth acetate	0.02
Toluene	15
Non-ionic surfactants	20
Water	64.96

#### Example 4.—Solid composition

25 Diatomaceous earth	80
Triphenylbismuth dihydroxide	20

Illustrative useful compositions containing highly preferred active bismuth compounds  $RBiX_2$  are Examples 5-8.

#### Example 5.—Aerosol composition

	Parts by weight
Tributyltin oxide	0.02
35 Butylbismuth dichloride	0.02
Toluene	15.00
Fluorohydrocarbon gaseous propellant	84.96

#### Example 6A.—Liquid composition

40 Butylbismuth dichloride	1
Water	8
Acetone	2
Lauryl dimethylbenzylammonium chloride (50%—in water)	10
45 Trisodium salt of N-hydroxyethylethylenediamine triacetic acid	0.4
Toluene	3

#### Example 6B

50 Another particularly desirable composition which may be employed using a quaternary ammonium compound may be:

Butylbismuth dichloride	1
Water	8
55 Acetone	2
Dodecyl pyridinium ammonium chloride (50%—in water)	10
Trisodium salt of N-hydroxyethylethylenediamine triacetic acid	0.4
60 Toluene	3

#### Example 7.—Emulsion composition

Tripropyltin acetate	0.02
Propylbismuth diacetate	0.02
65 Toluene	15.00
Non-ionic surfactants	20
Water	64.96

#### Example 8.—Solid composition

70 Diatomaceous earth	80
Octylbismuth diphenoxide	20

Plastics, textiles, paper products and paints are illustrative of the materials which are rendered resistant to attack when treated by applying the bismuth compound

to the surface and/or by incorporation therein. The plastics in massive and in fiber form include urethanes, halogenated polymers and copolymers such as polyvinyl chloride and polyvinyl chloride-acetate copolymers, polyesters, polyamides, polyolefins, and natural and synthetic rubbers. Natural fiber products that may be protected include paper products, hemp and felts. Paints may be protected "in the can" and also after application. Typical paints include interior and exterior vinyl latex and alkyd paints, the older non-synthetic flat natural paints, the acrylics, and the vinyls, and anti-fouling paints such as the acrylic and the vinyl varieties thereof. The bismuth compounds are also useful in preserving adhesives; in secondary oil recovery processes; in paper mill slime control processes; and in methods of controlling *Staphylococcus aureus* in hospitals. They may be a useful and active component of detergent sanitizers and may be used for this and other purposes in the form of an aerosol material. They may also be used to protect plants and other growth against attack by microorganisms. Illustrative of resistant paint compositions are Examples 9-14.

Example 9.—Acrylic anti-fouling paint

	Parts by weight
Titanium dioxide	160
Aluminum silicate	48
Talc	12
Methyl methacrylate-butyl methacrylate copolymer (40% in thinner)	433
Mineral spirits	148
Dibutylbismuth acetate	50

Example 10.—Vinyl anti-fouling paint

Titanium dioxide	150
Bentonite	14
Tricresyl phosphite	10
Vinyl chloride-vinyl acetate copolymer resin	102
Toluene	223
Methyl isobutyl ketone	295
Triphenylbismuth dichloride	35
Phenylbismuth dichloride	35

Example 11.—Flat interior paint

Titanium-calcium pigment	625
Calcium carbonate	100
Magnesium silicate	25
Ester gum solution (60% non-volatile in mineral spirits)	30
Bodied linseed oil	200
Mineral spirits	167
Cobalt naphthenate (6% Co)	1
Lead naphthenate (24% Pb)	2
Phenylbismuth dilaurylmercaptide	6

Example 12.—Acrylic anti-fouling paint

Titanium dioxide	160
Aluminum silicate	48
Talc	12
Methyl methacrylate-butyl methacrylate copolymer (40% in thinner)	433
Mineral spirits	148
Butylbismuth dichloride	50

Example 13.—Vinyl anti-fouling paint

Titanium dioxide	150
Bentonite	14
Tricresyl phosphite	10
Vinyl chloride-vinyl acetate copolymer resin	102
Toluene	223
Methyl isobutyl ketone	295
Triphenylbismuth dichloride	35
Butylbismuth diacetate	35

Example 14.—Flat interior paint

Titanium-calcium pigment	625
Calcium carbonate	100
Magnesium silicate	25
Ester gum solution (60% non-volatile in mineral spirits)	30
Bodied linseed oil	200
Mineral spirits	167
Cobalt naphthenate (6% Co)	1
Lead naphthenate (24% Pb)	2
Octylbismuth dilaurylmercaptide	6

In each of Examples 15-21, tests are reported showing the activity of the bismuth compounds against noted microorganisms, using the potent and toxic phenylmercury acetate as a standard (Example 22). In each example, a series of tests were carried out when the compound was placed within a nutrient broth in amount of 500, 250, 125, 63, 31, 16, 8, 4 and 2 parts per million (p.p.m.). Each broth was inoculated with the test organism and the broth incubated at 37° C. for two days. The organism growth was visually observed. The broth containing the minimum concentration which caused complete inhibition of the growth of the organism is tabulated.

Example	Compound	<i>Staph. aureus</i> , p.p.m.	<i>Aerobacter aerogenes</i> , p.p.m.	<i>Pseudomonas aeruginosa</i> , p.p.m.
15	Triphenylbismuth dichloride.	8	31	31
16	Triphenylbismuth sulfide (crude).	16	125	250
17	Triphenylbismuth diacetate.	1	8	16
18	Triphenylbismuth dimethacrylate.	1	31	63
19	Diphenylbismuth chloride.	<2	4	4
20	Phenylbismuth dichloride.	<2	<2	<2
21	Butylbismuth dichloride.	0.5	0.5	2
22	Phenylmercury acetate.	0.5	4	8

In each of Examples 23-26, tests are reported showing the activity of the bismuth compounds against the noted microorganisms. In each example the compound was tested using the Agar Diffusion Test, as follows: The test compounds were diluted in acetone to obtain the following stock solutions—5, 2.5, 1.25, 0.63, 0.31%. Filter paper discs, 10 mm. in diameter, were dipped in the test solution and the solvent then allowed to evaporate. AATCC Bacteriostasis agar, held at 45° C., was inoculated to 1% with an 18-24 hour nutrient broth culture of *Staph. aureus* or *E. coli*. The seeded agar was distributed at the rate of 15 ml./10 cm. Petri dish and allowed to solidify. The treated filter paper discs were placed on the seeded agar. Then the plates were incubated at 37° C. for 48 hours. Inhibition was determined by a zone or halo adjacent to the treated disc.

EXAMPLE 23

[Zones of inhibition in mm.]

	Percent solution	<i>S. aureus</i> , mm.	<i>E. coli</i> , mm.
Triphenylbismuth dichloride	2.5	5.5	2
	1.25	5	1
	0.63	5	1
	0.31	4	10
	0.16	3	0
	0.08	3	0
	0.04	2	0
	0.02	2	0
	0.01	20	0

EXAMPLE 24

Triphenylbismuth dichloride.....	5.0	9	3
	2.5	9	1
	1.25	9	1
	0.63	9	0
	0.31	8	0

EXAMPLE 25

Phenylbismuth dichloride.....	5	15	9
	2.5	13	8
	1.25	14	8
	0.63	13	6

EXAMPLE 26

Diphenylbismuth chloride.....	2.5	14	7
	1.25	13	4
	0.63	13	7
	0.31	13	5

<sup>1</sup> Partial.    <sup>2</sup> Partial zone.

In each of Examples 27-31, a urethane foam containing one of the bismuth compounds was tested against *Staph. aureus* in the Agar Diffusion Test. The foam composition and results follow:

Example		Parts by weight	Zone of inhibition, mm.
	Polyglycol ether.....	100	-----
	Polysiloxane.....	1	-----
	Stannous soap.....	0.45	-----
	N-ethylmorpholine.....	0.3	-----
	Triethylene diamine.....	0.1	-----
	Water.....	2.9	-----
	Toluene diisocyanate.....	38.6	-----
27.....	Triphenylbismuth dichloride.....	0.25	4
28.....	Diphenylbismuth chloride.....	0.1	5-6
29.....	do.....	0.05	5-6
30.....	Phenylbismuth dichloride.....	0.1	5-6
31.....	do.....	0.05	5-6

In each of Examples 32-33, a flexible polyvinyl chloride plastic containing the specified amount of triphenylbismuth dichloride was tested against *Staph. aureus* in the Agar Diffusion Test.

Example		Parts by weight	Zone of inhibition, mm.
	Stearic acid.....	0.25	-----
	Diethylphthalate.....	50	-----
	Polyvinyl chloride resin (Med. molecular weight). Barium-cadmium salt stabilizer.	100	-----
32.....	Triphenylbismuth dichloride.....	1	3
33.....	do.....	0.5	1.5

In each of Examples 34 and 35, polyvinyl chloride samples with the same formulation as in Examples 32 and 33, were prepared containing 1 part and 0.5 part of triphenylbismuth dichloride respectively. They were tested for activity against fungi as follows: 1¼" squares of the plastic, including a plastic control containing none of the bismuth compounds, were placed in Petri dishes containing 30 ml. of a mineral salt Agar. The plastic squares were inoculated with 0.5 ml. of a mixed spore suspension of *Aspergillus niger*, *Aspergillus flavus*, *Trichoderma* sp., and *Penicillium piscarium*. The inoculated samples were incubated at 30° C. for 14 days and then visually (and microscopically) examined for fungal growth. There was no growth on the samples prepared with the noted amounts of the bismuth compound. The plastic control exhibited moderate growth.

The following compounds are given as further examples of bismuth compounds employed in the compositions and methods of the invention and it will be understood that such compounds (as well as the other compounds

herein set forth) may be used in place of the various compounds specifically shown in the foregoing examples.

- Triphenylbismuth sulfide
- Triphenylbismuth diacetate
- Triphenylbismuth dimethacrylate
- Triphenylbismuth oxide
- Triphenylbismuth difluoride
- Triphenylbismuth dibromide
- Triphenylbismuth dihydroxide
- Triphenylbismuth (hydroxy)chloride
- Triphenylbismuth (chloro)acetate
- Triphenylbismuth dicyanide
- Trianisylbismuth dichloride
- Tribromophenylbismuth dichloride
- Tichlorophenylbismuth dichloride
- Tri- $\alpha$ -naphthylbismuth dichloride
- Trinitrophenylbismuth dichloride
- Tritolylbismuth dichloride
- Trixylylbismuth dibromide
- Tribiphenylbismuth dichloride
- Diphenyl-p-tolylbismuth dichloride
- Tri-p-tolylbismuth diacetate
- Triphenylbismuth dibenzoate
- Triphenylbismuth mercaptopropionate
- Tri-p-tolylbismuth dibenzoate
- Tri-o-tolylbismuth disalicylate  $\cdot$  C<sub>6</sub>H<sub>6</sub>
- Triphenylbismuth disalicylate
- Triphenylbismuth di-p-hydroxybenzoate
- Triphenylbismuth di-p-aminobenzoate
- Triphenylbismuth di-p-aminobenzoate  $\cdot$  2CH<sub>3</sub>COCH<sub>3</sub>
- Triphenylbismuth dichloroacetate
- Triphenylbismuth ditartrate
- Triphenylbismuth diphenoxide
- Triphenylbismuth dilaurylmercaptide
- Triphenylbismuth dibutoxide
- Tritolylbismuth di-o-phenylphenate
- Tritolylbismuth S,S'-bis isooctylmercaptoacetate
- Tritolylbismuth diethoxide
- Octylbismuth sulfide
- Butylbismuth sulfide
- Dibutylbismuth acetate
- Butylbismuth dibenzoate
- Dibutylbismuth methacrylate
- Butylbismuth diacrylate
- Dibutylbismuth phenate
- Butylbismuth mercaptopropionate
- Dibutylbismuth laurylmercaptide
- Dibutylbismuth isooctylmercaptoacetate
- Butylbismuth bis-o-phenylphenate
- Diphenylbismuth chloride
- Di-p-chlorophenylbismuth chloride
- Di-p-chlorophenylbismuth bromide
- Di-p-chlorophenylbismuth iodide
- Diphenylbismuth chloride
- Diphenylbismuth iodide
- Diphenylbismuth cyanide
- Diphenylbismuth hydroxide
- Diphenylbismuth thiocyanate
- Di-p-tolylbismuth chloride
- Dicyclohexylbismuth chloride
- Cyclopentylbismuth diacetate
- Vinylphenylbismuth dichloride
- Phenylbismuth dibromide
- p-Chlorophenylbismuth dibromide
- p-Tolylbismuth dichloride
- Diethylbismuth bromide
- Dibutenylbismuth chloride
- Diallylbismuth acetate
- Dimethylbismuth chloride
- Vinylbismuth dichloride
- Dimethylbismuth hydroxide
- Methylbismuth dichloride
- Methylbismuth oxide
- Butylbismuth sulfide

Butylbismuth oxide  
 Ethylbismuth dichloride  
 Ethylbismuth dichloride  
 Butylbismuth dibromide  
 Dibutylbismuth cyanide

Those skilled in the art will appreciate that other organobismuth compounds as defined herein can be employed in the compositions and methods of the invention to protect a wide variety of materials and living organisms that are susceptible to attack by microorganisms.

As is well known to those skilled in the art, the compounds which may be used in practice of this invention may be synthesized by well known techniques and are readily obtainable. As many embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention includes all such modifications as come within the scope of the appended claims.

I claim:

1. A method for protecting a medium susceptible to attack by microorganisms which comprises applying to the locus to be protected an effective amount of a bismuth compound  $\text{RBiX}_2$  wherein X is selected from the group consisting of halogen, oxygen, sulfur, carboxylate, phenoxide, alkoxide, mercaptide, and cyanide, and R is lower alkyl.

2. A method for protecting a medium susceptible to attack by microorganisms as claimed in claim 1 wherein R is butyl.

3. A method for protecting a medium susceptible to attack by microorganisms as claimed in claim 1 wherein X is chloride.

4. A method for protecting a medium susceptible to attack by microorganisms as claimed in claim 1 wherein the bismuth compound  $\text{RBiX}_2$  is butylbismuth dichloride.

5. A method for protecting a medium susceptible to attack by microorganisms which comprises applying to the locus to be protected an effective amount of (a) a bismuth compound  $\text{RBiX}_2$  wherein X is selected from the group consisting of halogen, oxygen, sulfur, carboxylate, phenoxide, alkoxide, mercaptide, and cyanide, and R is lower alkyl; and (b) a compound  $\text{R''}_c\text{NH}_d\text{A}$  wherein  $\text{R''}$  is a hydrocarbon radical, A is an anion of a complex-forming acid, c is an integer 1-4, d is an integer 0-3, and the sum of c and d is 4.

6. A composition comprising an inert carrier, as the active component a bactericidal amount of 0.02%-20% by weight of a bismuth compound  $\text{RBiX}_2$  wherein X is selected from the group consisting of halogen, oxygen, sulfur, carboxylate, phenoxide, alkoxide, mercaptide, and cyanide, and R is lower alkyl, and a dispersing agent.

7. A composition as claimed in claim 6 wherein R is butyl.

8. A composition as claimed in claim 6 wherein X is chloride.

9. A composition as claimed in claim 6 wherein the bismuth compound  $\text{RBiX}_2$  is butylbismuth dichloride.

10. A composition comprising a carrier and, as the active component a bactericidal amount of (a) 0.1%-10% by weight of a bismuth compound  $\text{RBiX}_2$  wherein X is selected from the group consisting of halogen, oxygen, sulfur, carboxylate, phenoxide, alkoxide, mercaptide, and cyanide, and R is lower alkyl; and (b) a compound  $\text{R''}_c\text{NH}_d\text{A}$  wherein  $\text{R''}$  is a hydrocarbon radical, A is an anion of a complex-forming acid, c is an integer 1-4, d is an integer 0-3, and the sum of c and d is 4.

11. A composition comprising an inert carrier, as the active component 0.1%-10% by weight of a bismuth compound  $\text{RBiX}_2$  wherein X is selected from the group consisting of halogen, oxygen, sulfur, carboxylate, phen-

oxide, alkoxide, mercaptide, and cyanide, and R is lower alkyl, and a dispersing agent.

12. A microorganism resistant paint comprising a paint composition and an effective amount of a bismuth compound  $\text{RBiX}_2$  wherein X is selected from the group consisting of halogen, oxygen, sulfur, carboxylate, phenoxide, alkoxide, mercaptide, and cyanide, and R is lower alkyl.

13. A microorganism resistant paint as claimed in claim 12 comprising a paint composition and an effective amount of butylbismuth dichloride.

14. A microorganism resistant plastic material comprising a plastic composition and an effective amount of a bismuth compound  $\text{RBiX}_2$  wherein X is selected from the group consisting of halogen, oxygen, sulfur, carboxylate, phenoxide, alkoxide, mercaptide, and cyanide, and R is lower alkyl.

15. A microorganism resistant urethane comprising a urethane and an effective amount of a bismuth compound  $\text{RBiX}_2$  wherein X is selected from the group consisting of halogen, oxygen, sulfur, carboxylate, phenoxide, alkoxide, mercaptide, and cyanide, and R is lower alkyl.

16. A microorganism resistant paper comprising paper and an effective amount of a bismuth compound  $\text{RBiX}_2$  wherein X is selected from the group consisting of halogen, oxygen, sulfur, carboxylate, phenoxide, alkoxide, mercaptide, and cyanide, and R is lower alkyl.

17. A microorganism resistant cloth comprising cloth and an effective amount of a bismuth compound  $\text{RBiX}_2$  wherein X is selected from the group consisting of halogen, oxygen, sulfur, carboxylate, phenoxide, alkoxide, mercaptide, and cyanide, and R is lower alkyl.

18. A bacteriostatic aerosol composition comprising a carrier, a propellant, and as the active component a bismuth compound  $\text{RBiX}_2$  wherein X is selected from the group consisting of halogen, oxygen, sulfur, carboxylate, phenoxide, alkoxide, mercaptide, and cyanide, and R is lower alkyl.

19. A method of treating a hospital to minimize the incidence of *Staph. aureus* which comprises applying to filters, room surfaces, and cloth an effective amount of a bismuth compound  $\text{RBiX}_2$  wherein X is selected from the group consisting of halogen, oxygen, sulfur, carboxylate, phenoxide, alkoxide, mercaptide, and cyanide, and R is lower alkyl.

20. A composition comprising a solid inert carrier and, as the active component a germicidal amount of a bismuth compound  $\text{RBiX}_2$  wherein X is selected from the group consisting of halogen, oxygen, sulfur, carboxylate, phenoxide, alkoxide, mercaptide, and cyanide and R is lower alkyl.

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