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3,408,298

DETERGENT GERMICIDAL COMPOSITIONS

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No Drawing. Original application Aug. 18, 1965, Ser. No. 480,763. Divided and this application Mar. 11, 1966, Ser. No. 533,401

9 Claims. (Cl. 252-107)

This application is a division of my copending application Serial No. 480,763, filed August 18, 1965, for complexes of quaternary phenates, derivatives thereof, and germicidal detergent compositions thereof.

This invention relates to new complex compounds which have extremely effective bacteriocidal, germicidal and fungicidal activity, including a tuberculocidal activity. The compounds of the present invention having these extremely important properties are quaternary ammonium substituted phenate halide complexes.

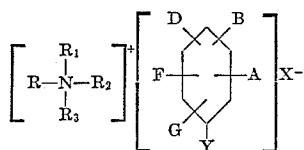
It is a primary object of the present invention, to provide new quaternary ammonium complex compounds having bacteriocidal, fungicidal, germicidal, and tuberculocidal activity.

It is another object of the present invention to provide new quaternary ammonium substituted phenate halide complexes which have these properties and which can be used in various types of formulations so as to achieve these effects.

It is yet another object of the present invention to provide these complex compounds with a high degree of effectiveness as bacteriocidal, fungicidal and germicidal agents, which have the additional advantage of not causing any skin irritation so that the same can be used for all of these purposes where they come into contact with the skin.

Other objects and advantages of the present invention will be apparent from a further reading of the specification and of the appended claims.

With the above and other objects in view, the present invention mainly comprises a quaternary ammonium complex of the formula:



wherein R is selected from the group consisting of alkyl of 8-24 carbon atoms, dodecylbenzyl, o-, m- and p-octyl phenoxy ethoxy ethyl, wherein R₁ alone is alkyl of up to 24 carbon atoms (preferably lower alkyl such as methyl, ethyl, propyl, butyl or amyl), phenyl, chlorophenyl, bromophenyl, alkyl-phenyl, (preferably lower alkylphenyl), benzyl, alkyl-benzyl (preferably lower alkyl-benzyl such as methylbenzyl, ethylbenzyl, propyl-benzyl, butylbenzyl or amylbenzyl), di-alkylbenzyl (preferably di-lower alkyl benzyl such as dimethylbenzyl, diethylbenzyl, dipropylbenzyl, dibutylbenzyl or diamylbenzyl), chlorobenzyl, dichlorobenzyl, bromobenzyl, dibromobenzyl, naphthyl-lower alkyl (preferably naphthyl-methyl or naphthylethyl) and alkyl naphthyl ammonium chloride wherein the alkyl is from 8-24 carbon atoms and is preferably a mixture of C₁₁ and C₁₂, most preferably C₁₂ 98% and C₁₁ 2%, wherein R₂ alone is lower alkyl (preferably methyl or ethyl), wherein R₃ alone is lower alkyl (preferably methyl or ethyl), wherein R₁ together with one of the groups R₂ and R₃ is selected from the group consisting of morpholinyl, methylmorpholinyl and piperidinyl, and wherein R₁, R₂ and R₃ together is selected from the group consisting

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of pyridinyl, lower alkyl-substituted pyridinyl wherein the lower alkyl is preferably methyl, ethyl, propyl, butyl, or amyl, benzyl-substituted pyridinyl, quinolinyl, and isoquinolinyl, wherein A, B, D and F are each selected from the group consisting of hydrogen, lower alkyl (preferably methyl, ethyl, propyl, butyl or amyl), chlorine, bromine, iodine, phenyl, lower alkyl-phenyl (preferably methyl, ethyl, propyl, butyl or amyl phenyl), lower alkoxy-phenyl (preferably methyloxy, ethyloxy, propyloxy, butyloxy or amyloxy-phenyl), chlorophenyl, bromophenyl, benzyl, lower alkyl-benzyl, lower alkoxy-benzyl, chlorobenzyl and bromobenzyl, wherein G can be any of the substituents given for A, B, D or F, with the exception of hydrogen, wherein Y is selected from the group consisting of oxygen and sulfur, and wherein X is selected from the group consisting of chlorine, bromine, and iodine.

The complexes of the present invention may be formed by reacting an alkali metal or ammonium substituted phenate or thiophenate with the chosen quaternary ammonium halide and with the chosen halogen.

The complexes of the present invention include the halogen complexes of the above mentioned quaternary ammonium adducts of the following phenols: o-, m-, and p-phenyl phenol, alkylated phenols such as o-, m- and p-cresols, xylenols and higher analogs such as o-ethyl phenyl, p-propyl phenol, m-butyl phenol and the like, aralkylated phenols such as o-, m- and p-benzyl phenols, halogenated phenols such as the following chlorinated phenols:

- (a) Monochloro (ortho, meta, para)
- (b) Dichloro (1,2; 1,3; 1,4; 1,5; 2,3; 2,4; 3,4)
- (c) Trichloro (1,2,3; 1,2,4; 1,2,5; 2,3,4; 2,3,5; 3,4,5)
- (d) Tetrachloro (1,2,3,4; 1,2,3,5; 1,2,4,5)
- (e) Pentachloro (1,2,3,4,5)

as well as the brominated and iodinated phenols such as orthobromo phenol, 1,3-dibromo phenol, meta-iodo phenol, 1,2,4-triodo phenol, penta bromo phenol, and the like, alkylated halogenated phenols such as chloro-cresols, chloro-xylenols, bromo-cresols, bromo-xylenols, iodo-cresols, iodo-xylenols, and halogenated higher analogs, as well as halogenated benzyl phenols which may be halogenated on the benzyl or on the phenol by chlorine, bromine or iodine.

It is to be understood that in place of any of the above phenols it is possible to substitute the corresponding thiophenol.

Among the suitable quaternary ammonium halides which may be reacted with the alkali metal or ammonium substituted phenates or thiophenates in accordance with the present invention are halides such as chlorides, bromides and iodides of the following:

Dodecyl trimethyl ammonium as well as other higher alkyl trimethyl ammoniums such as alkyls of 14, 16, 18, 20, 22 or 24 carbon atoms;

Dodecyl dimethyl benzyl ammonium as well as other higher alkyl derivatives instead of the dodecyl such as alkyls of 14, 18 or 20 carbon atoms;

Dodecyl dimethyl chlorobenzyl ammonium;

Dodecyl dimethyl dichlorobenzyl ammonium;

Dodecyl dimethyl methylbenzyl ammonium;

Dodecyl dimethyl dimethylbenzyl ammonium;

Dodecyl dimethyl ethylbenzyl ammonium;

Dodecyl dimethyl naphthylmethyl ammonium;

Dodecylbenzyl trimethyl ammonium;

Dodecylbenzyl triethyl ammonium;

Dodecyl dimethyl propylbenzyl ammonium;

Dodecyl dimethyl butylbenzyl ammonium; and

Didodecyl dimethyl ammonium.

In all of the above, wherever dodecyl is mentioned, it is to be understood that another higher alkyl can be sub-

stituted for the dodecyls such as alkyls of 14, 16, 18, 20, 22 or 24 carbon atoms, or the like.

It is to be understood that instead of dodecyl in quaternary ammonium halides of the above and similar type such as dodecyl dimethyl ethyl ammonium chloride, the higher alkyls need not be of even number (e.g. alkyls of 11, 13, 15, 17 or 19 carbon atoms also being suitable), and in addition, the higher alkyls need not be saturated and can, for example, be oleyl, linoleyl, linolenyl, or the like, such as in the case of oleyl dimethyl ethyl ammonium bromide.

As indicated above, in the case of the quaternary ammonium halide it is possible for R_1 together with either R_2 or R_3 to form a saturated heterocyclic radical such as morpholinyl, methyl morpholinyl, or piperidinyl, resulting in such quaternary ammonium halides as dodecyl ethyl morpholinyl ammonium bromide, dodecylbenzyl ethyl methylmorpholinyl ammonium chloride and stearyl methyl piperidinyl ammonium iodide.

It is also possible for R_1 , R_2 and R_3 together with the nitrogen atom to form an unsaturated heterocyclic radical such as pyridinyl, alkyl or aralkyl substituted pyridinyl (e.g. the pyridine ring substituted with a methyl, ethyl, propyl, butyl, or benzyl radical), quinolinyl, and the like. Among the suitable quaternary ammonium halides may be mentioned dodecyl pyridinyl ammonium chloride, dodecylbenzyl methyl pyridinyl ammonium bromide, dodecyl quinolinyl ammonium iodide, dodecylbenzyl isoquinolinyl ammonium chloride, etc.

In addition, the quaternary ammonium halides include alkylphenoxyethoxyethyl dimethyl benzyl ammonium halides wherein the alkyl is preferably of 8-20 carbon atoms, such as p-octylphenoxyethoxyethyl dimethyl benzyl chloride.

The complexes of the present invention are either completely water insoluble or only very slightly soluble (immiscible or slightly miscible). They have a high bacteriocidal, germicidal and fungicidal action. Their germicidal efficiency is high against both gram positive and gram negative organisms, and because of the fact that they have no toxicity and do not cause any skin irritation, they can be used in skin preparations and in preparations which are sprayed on objects which may come in contact with the skin, for example in preparations which are sprayed on mattresses to destroy undesired organisms.

The complexes of the present invention have been found effective against such gram positive organisms as *Staphylococcus pyogenes aureus*, such gram negative organisms as *Salmonella typhosa*, *Salmonella choleraesuis*, *Pseudomonas aeruginosa*, and *Proteus vulgaris*, and such spore formers as *Bacillus subtilis*, *Clostridium sporogenes* and *Aspergillus niger*. Other organisms against which the complexes of the present invention have been found to be effective include *M. albicans*, *B. proteus*, *S. albus*, bacterial flora, *streptococci*, *B. mycoides*, and many others, as well as various fungi such as mildew. The complexes have also been found to be effective against *Mycobacterium tuberculosis*.

It is important to note that tests carried out with the quaternary ammonium complexes of the present invention prove that the same do not merely inhibit the growth of the tested organisms, but actually kills the same.

The quaternary ammonium complexes of the present invention are compatible with all types of detergents, that is non-ionic detergents, cationic detergents and anionic detergents.

These complexes are compatible with all non-ionic detergents, including alkyl phenoxy polyethoxy ethanol (4 to 20 units of ethoxy) ethoxy alcohols (wherein the alcohol is of 12-18 carbon atoms and there are from 6-25 ethoxy units), ethoxylated acids (wherein there are 6-20 ethoxy units and wherein the acid is of 12-18 carbon atoms), ethoxylated alkyl thiols (wherein the alkyl is of 8-16 carbon atoms, and wherein there are 6-20 ethoxy units), etc.

The quaternary ammonium complexes of this invention are also compatible with all cationic detergents, such as: cetyl pyridinium chloride, alkyl dimethyl benzyl ammonium chloride, lauryl isoquinolinium bromide, alkyl trimethyl ammonium chloride, di-stearyl dimethyl ammonium chloride; alkenyl, ethyl ethanol imidazolinium bromide; di-octyl phenoxy ethoxy ethyl dimethylbenzyl ammonium chloride; stearyl amido propyl trimethyl ammonium chloride; alkenyl trimethyl ammonium chloride; dodecyl benzyl trimethyl ammonium chloride; etc.

It is a particular advantage of the present invention, and most surprising, that the quaternary ammonium complexes of this invention are compatible with anionic detergents so that it is possible to make effective detergent germicidal preparations which can be safely contacted with the skin. Among the suitable anionic detergents are dodecylbenzene sulfonates which may be solvated by alkanolamides, soaps coupled with alkaknolamides and sodium salts of complex organic phosphate esters, dodecyl sodium sulfate, dodecyl ammonium sulfate, dodecyl triethanolamine sulfate, myristyl sodium sulfate, myristyl ammonium sulfate, myristyl triethanolamine sulfate, palmityl sodium sulfate, palmityl ammonium sulfate, palmityl triethanolamine sulfate, stearyl sodium sulfate, stearyl ammonium sulfate, stearyl triethanolamine sulfate, lauryl polyethoxy sodium sulfate wherein ethoxy is 1 to 6 units; and the same from myristyl, palmityl and stearyl; saturated sodium, ammonium and potassium soaps such as lauryl stearate, palmitates, etc.

Because of their water insolubility and substantivity the complexes of the present invention can serve as mold inhibitors on textiles, leather, rope and paper.

Among the various types of preparations that may be made with these complexes are liquid and aerosol spray germicides, detergent germicides of all types, for example for use as hospital decontaminants against gram positive and gram negative organisms. The preparations may also be used in motels, hotels, restaurants, homes, doctors' offices, dentists' offices, veterinarian establishments, kennels, public buildings such as schools, rest rooms, etc.

The following examples are given to illustrate the production of the complexes of the present invention. The scope of the invention is now, however, meant to be limited to the specific details of the examples.

EXAMPLE 1

452 grams of para-octyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride (Hyamine 1622) are dissolved in 1200 grams of isopropyl alcohol. There is added thereto dropwise, under agitation, 22.5 grams of bromine.

192 grams of sodium ortho phenyl phenate are dissolved in 526 grams of isopropyl alcohol. This alcoholic phenate solution is mixed with the alcoholic quaternary ammonium solution under agitation.

The formed sodium chloride is filtered off leaving a filtrate which is a 25% alcoholic solution of the formed paraoctyl phenoxy ethoxy ethyl dimethyl benzyl ammonium ortho-phenyl phenate bromine complex.

The method can also be carried out by mixing the 452 grams of para-octylphenoxyethoxy ethyl dimethyl benzyl ammonium chloride (Hyamine 1622) dissolved in 1200 grams of isopropyl alcohol with the 192 grams of sodium ortho phenyl phenate dissolved in 526 grams of isopropyl alcohol. The sodium chloride which is formed in the reaction is separated and to the remaining liquid is added dropwise, under agitation, 22.5 grams of bromine. This results in the formation of para-octyl phenoxy ethoxy ethyl dimethyl benzyl ammonium ortho-phenyl phenate bromine complex.

The same method can be carried out using 208 grams of sodium ortho-phenyl thiophenate instead of 192 grams of sodium ortho-phenyl phenate, to produce as the final product the corresponding para-octyl phenoxy ethoxy ethyl dimethyl benzyl ammonium ortho-phenyl thiophenate bromine complex.

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EXAMPLE 2

350 grams of anhydrous alkyl (C_8-C_{18}) dimethyl benzyl ammonium chloride are dissolved in 1050 grams of isopropyl alcohol. 17.5 grams of bromine are added there-
to dropwise. The resulting solution is mixed, under agita-
tion, with a solution of 192 grams of sodium ortho-phenyl
phenate dissolved in 526 grams of isopropyl alcohol.

The formed sodium chloride is filtered off, leaving a
filtrate which is a 25% alcoholic solution of alkyl
(C_8-C_{18}) dimethyl benzyl ammonium ortho-phenyl phe-
nate bromine complex.

EXAMPLE 3

350 grams of anhydrous dodecyl benzyl trimethyl am-
monium chloride are dissolved in 1050 grams of isopropyl
alcohol. 17.5 grams of iodine crystal are gradually added
thereto with adequate agitation. The resulting solution
is mixed with a solution of 192 grams of sodium ortho-
phenyl phenate dissolved in 600 grams of isopropyl alco-
hol.

The formed sodium halides are filtered off. The re-
sulting filtrate is a 25% solution of dodecyl benzyl tri-
methyl ammonium ortho-phenyl phenate iodine complex.
The complex may be recovered by evaporation of the
solvent under vacuum.

The complexes of the above examples contain 5%
halogens. The amount of complexed halogen can, how-
ever, vary from 0.1% to 15%, depending on the parent
complex and the use to which the final product is to be
put.

EXAMPLE 4

264.5 grams of anhydrous dodecyl trimethyl ammonium
chloride are dissolved in 794.5 grams of isopropyl alco-
hol. The resulting solution is mixed with a solution of 170
grams of ortho-phenyl phenol dissolved in 510 grams of
isopropyl alcohol. A 25% alcoholic solution of NaOH is
added under agitation. The formed sodium chloride is
filtered. 13.5 grams of chlorine is added to resultant fil-
trate. The chlorine is administered by bubbling the gas
through the alcoholic solution until the alcoholic mass
increases by 13.5 grams. The filtrate consists of a 25%
solution of dodecyl trimethyl ammonium ortho-phenyl
phenate chlorine complex.

The following are examples of some possible formula-
tions using the complexes of the present invention as
active ingredient.

EXAMPLE 5

An aerosol is prepared of:

- 1% of the complex of Example 1
- 3% isopropyl alcohol
- 1% propylene glycol
- 0.02% essential oils
- 3% methylene chloride
- 93% propellant (Freon 14).

EXAMPLE 6

A liquid spray is prepared:

- 4% of the solution of Example 2 (1% complex and
3% isopropyl alcohol)
- 1% propylene glycol
- 0.02% essential oils
- 94.8% methylene chloride.

EXAMPLE 7

A detergent germicidal preparation is prepared of the
following composition:

- 10% of the solution of Example 3 (2½ of the
complex, and 7½ % of isopropyl alcohol)
- 6% of an anionic detergent (sodium lauryl sulfate)
- 1% sequesterene
- 3% tripolyphosphate, and
- 3% trisodium phosphate.

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EXAMPLE 8

108 grams of para-cresol are dissolved in 1000 grams
of distilled water containing 40 grams of sodium hydrox-
ide. 760 grams of 50% alkyl (C_8-C_{18}) dimethyl benzyl
ammonium chloride is diluted to 1 liter with distilled
water. The resultant cresol solution and quaternary am-
monium solution are blended and the mass heated to near
boiling. The resultant organic top layer is separated and
dissolved in 99% isopropanol to make a 25% solids alkyl
dimethyl benzyl ammonium para-cresylate. To the cresol-
quaternary adduct alcoholic solutions is added 45 grams
of bromine dissolved in 135 grams of isopropanol. The re-
sultant product is 25% alkyl dimethyl benzyl ammonium
para-cresylate bromine complex containing 10% by weight
of bromine.

EXAMPLE 9

The same procedure is followed as in Example 8 sub-
stituting ortho-cresol for the para-cresol and resulting in
alkyl dimethyl benzyl ammonium ortho-cresylate bromine
complex.

By using meta-cresol the resulting product is alkyl di-
methyl benzyl ammonium meta-cresylate bromine com-
plex.

EXAMPLE 10

The same procedure is followed as in Example 9 using
sodium meta-phenyl phenate and resulting in the produc-
tion of alkyl dimethyl benzyl ammonium meta-phenyl
phenate bromine complex.

EXAMPLE 11

The same procedure is followed as in Example 3, how-
ever, using sodium para-phenyl phenate and resulting in
the production of dodecyl benzyl trimethyl ammonium
para-phenyl phenate iodine complex.

EXAMPLE 12

184 grams of benzyl phenol are dissolved in 1000 grams
of distilled water containing 40 grams of sodium hydrox-
ide. 760 grams of 50% alkyl (C_8-C_{18}) dimethyl benzyl
ammonium chloride are diluted to 1 liter with distilled
water. The resulting phenol solution and the quaternary
ammonium solution are blended and the mass heated to
near boiling. The resulting organic top layer is separated
and dissolved in 99% isopropanol to make a 25% solids
alkyl dimethyl benzyl ammonium benzyl phenate. To the
phenol-quaternary adduct alcoholic solutions is added 53
grams of bromine dissolved in 159 grams of isopropanol.
Depending on whether ortho- meta or para-benzyl phenol
was used to start with, the resulting product will be 25%
alkyl dimethyl benzyl ammonium (ortho, meta or para)
benzyl phenate bromine complex.

EXAMPLE 13

The same procedure is followed as in Example 12 using
128 grams of monochlorophenol with 40 grams of sodium
hydroxide, 410 grams of alkyl dimethyl naphthyl methyl
ammonium chloride in 1000 grams of hot water, and add-
ing 50 grams of bromine in 150 grams of isopropanol. De-
pending on whether ortho-, meta or para-monochlor phe-
nol is used to start with, the resulting product will be 25%
alkyl dimethyl naphthyl methyl ammonium (ortho, meta
or para) chloro phenate bromine complex.

EXAMPLE 14

The same procedure is followed as in Example 12 using
163 grams of 1,3-dichloro phenol, 780 grams of a 50%
solution of alkyl dimethyl benzyl ammonium chloride and
complexing with 50 grams of bromine in 150 grams of
isopropanol. The resulting product is alkyl dimethyl ben-
zyl ammonium dichloro-phenate bromine complex (10%
bromine).

EXAMPLE 15

197.5 grams of 1,2,4-trichloro phenol are dissolved in 1000 grams of distilled water containing 40 grams of NaOH. 776 grams alkyl (C_8-C_{18}) dimethyl ethyl benzyl ammonium chloride diluted to 1000 grams is added to the phenols and heated to boiling with agitation. The organic layer is separated and dissolved in isopropyl alcohol to make a 25% solids solution. 59 grams of bromine is added in 177 grams of isopropanol. The resultant alcoholic solution is a 25% alkyl dimethyl ethyl benzyl 1,2,4-trichloro phenate bromine complex.

EXAMPLE 16

292 grams of 1,2,3,5-tetrachloro phenol are dissolved in 2000 grams of water containing 40 grams of NaOH. 720 grams of 50% dodecyl trimethyl ammonium chloride are added and heated to boiling with agitation. The organic layer is separated and dissolved in isopropanol to make a 25% solid solution. 69 grams of bromine dissolved in 183 grams of isopropanol are added. The resultant product is a 25% solution of dodecyl trimethyl ammonium 1,2,3,5-tetrachlorophenate bromine complex containing 10% bromine.

EXAMPLE 17

266 grams of pentachloro phenol are dissolved in 2000 grams of distilled water containing 40 grams of sodium hydroxide. 640 grams of 50% cetyl trimethyl ammonium chloride are added. The resultant solution is heated to 210° F. with agitation. The resultant solution is evaporated to dryness. The residue is taken up with isopropanol and the NaCl filtered off. The solids are adjusted to 25% and a 25% alcoholic bromine solution added to give a resultant product of a 25% cetyl trimethyl ammonium pentachloro phenate bromine complex.

EXAMPLE 18

146 grams of 1,5-dimethyl-4-chloro phenol are dissolved in 2000 grams of water containing 40 grams of sodium hydroxide. To this solution is added 780 grams of 50% alkyl dimethyl benzyl ammonium chloride. The resultant solution is heated with agitation to 210° F. The organic layer is separated and dissolved in isopropanol to prepare a 25% solid solution. 49 grams of bromine dissolved in 147 grams of alcohol (isopropanol) are added. The resultant solution is a 25% alkyl dimethyl benzyl 1,5-dimethyl-4-chloro phenate bromine complex containing 10% bromine.

EXAMPLE 19

218 grams of para-chloro-ortho-benzyl phenol are dissolved in 2000 grams of water containing 40 grams of sodium hydroxide. 900 grams of a 50% solution of para-octyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride is added and resultant solution heated with agitation to 210° F. The organic layer is separated and dissolved in alcohol to make a 25% solution. 63 grams of bromine dissolved in 189 grams of alcohol are added. The resultant product is a 25% solution of para-octyl phenoxy ethoxy ethyl dimethyl benzyl ammonium para-chloro-ortho-benzyl phenate bromine complex.

EXAMPLE 20

Preparation of dodecyl dimethyl naphthyl methylammonium ortho phenyl phenate iodine complex

40 grams of dodecyl dimethyl naphthyl methyl ammonium chloride were dissolved in 250 grams of 99% isopropyl alcohol. 19.2 grams of sodium ortho phenyl phenate were dissolved in 250 grams of 99% isopropyl alcohol. The alcoholic phenate solution was added to the alcoholic quaternary ammonium solution with adequate agitation. The mixture was allowed to stand two hours and the resultant salt removed by filtration. To the filtrate, 5.3 grams of iodine crystals were slowly added with vigorous agitation. The resultant solution was do-

decyl dimethyl naphthyl methyl ammonium ortho phenyl phenate iodine complex, in 10% concentration.

EXAMPLE 21

Preparation of dodecyl para butyl pyridinium para chloro ortho benzyl phenate bromine complex

43.1 grams (0.1 mol) of dodecyl para butyl pyridinium iodide were dissolved in 250 grams of 99% isopropyl alcohol. 24 grams of sodium para chloro ortho benzyl phenate was dissolved in 250 grams of isopropyl alcohol. The alcoholic phenate solution was added to the alcoholic quaternary ammonium solution with good agitation. The resultant mixture was allowed to stand two hours and the resultant salt removed by filtration. 6.1 grams of bromine were added dropwise to the filtrate with vigorous agitation. The resultant solution was further diluted with isopropyl alcohol to 610 grams to make a 10% solution of dodecyl para butyl pyridinium para chloro ortho benzyl phenate bromine complex.

EXAMPLE 22

Preparation of tetradecyl dimethyl dichlorobenzylammonium para benzyl phenate bromine complex

43.6 grams of tetradecyl dimethyl dichlorobenzyl ammonium chloride were dissolved in 250 grams of isopropanol. 20.6 grams of sodium para benzyl phenate were dissolved in 250 grams of isopropanol. The alcoholic phenate solution was added to the alcoholic quaternary ammonium solution with adequate agitation. The mixture was allowed to stand two hours and the salt was removed by filtration. 5.8 grams of bromine were added dropwise with vigorous agitation to the filtrate. The resultant mixture was approximately 10% tetradecyl dimethyl dichlorobenzyl ammonium para benzyl phenate bromine complex.

EXAMPLE 23

Preparation of dodecyl benzyl isoquinolinium metal cresolate iodine complex

43.5 grams of dodecyl benzyl isoquinolinium chloride were dissolved in 250 grams of isopropanol. 13 grams of sodium metal-cresolate were dissolved in 250 grams of isopropyl alcohol. The alcoholic cresolate solution was added with adequate agitation to the alcoholic quaternary ammonium solution. The resultant mixture was allowed to stand two hours. The salt produced was removed by filtration. 5.1 grams of iodine were added to the filtrate. This produced a 10% solution of dodecyl benzyl isoquinolinium meta cresolate iodine complex.

EXAMPLE 24

Preparation of octadecyl pyridinium para tertiary butyl phenate bromine complex

41.2 grams of octadecyl pyridinium bromide were dissolved in 250 grams of 99% isopropyl alcohol. 17.2 grams of sodium para tertiary butyl phenate were dissolved in 250 grams of 99% isopropyl alcohol. The alcoholic phenate solution was added to the alcoholic quaternary ammonium solution with good agitation. The resultant solution was allowed to stand 2-3 hours and the salt formed removed by filtration. 5.2 grams of bromine was added dropwise to the filtrate with vigorous agitation. The resultant solution is 10% octadecyl pyridinium para tertiary butyl phenate bromine complex, containing 10% by weight of bromine.

EXAMPLE 25

Preparation of dodecyl ethyl morpholinium ortho phenyl phenate bromine complex

36.4 grams (0.1 mol) of dodecyl ethyl morpholinium bromide were dissolved in 250 grams of 99% isopropyl alcohol. 19.2 grams of sodium ortho phenyl phenate were

dissolved in 250 grams of 99% isopropyl alcohol. The alcoholic phenate solution was added to the alcoholic quaternary ammonium solution with adequate agitation. The result mixture was allowed to stand for a few hours and the salt formed was removed by filtration. 4.9 grams of bromine were added to the resultant filtrate dropwise with vigorous agitation. The resultant solution contains 10% of dodecyl ethyl morpholinium ortho phenyl phenate, containing 10% complexed bromine.

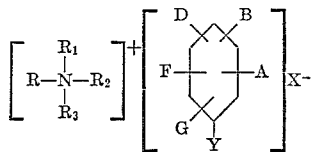
EXAMPLE 26

Using any of the products of Examples 8-25, aerosols, liquid sprays and detergent germicidal preparations of Examples 5-7 can be prepared.

Without further analysis, the foregoing will so fully reveal the gist of the present invention that others can, by applying current knowledge, readily adapt it for various applications without omitting features that, from the standpoint of prior art, fairly constitute essential characteristics of the generic or specific aspects of this invention and, therefore, such adaptations should and are intended to be comprehended within the meaning and range of equivalence of the following claims.

What is claimed as new and desired to be secured by Letters Patent, is:

1. A detergent germicidal composition consisting essentially of an organic detergent selected from the group consisting of alkyl phenoxy polyethoxy ethanol containing 4 to 20 ethoxy units, ethoxy alcohols wherein the alcohol is of 12-18 carbon atoms and containing 6-25 ethoxy units, ethoxy acids containing 6-20 ethoxy units and wherein the acid is of 12-18 carbon atoms, ethoxy alkyl thiols containing 6-20 ethoxy units and wherein the alkyl is of 8-16 carbon atoms, cetyl pyridinium chloride, alkyl dimethyl benzyl ammonium chloride, lauryl isoquinolinium bromide, N-alkyl trimethyl ammonium chloride, di-stearyl dimethyl ammonium chloride, alkenyl, ethyl and ethanol imidazolinium bromide, dioctyl phenoxy ethoxy ethyl dimethyl ammonium chloride, stearyl amido propyl trimethyl ammonium chloride, alkenyl trimethyl ammonium chloride, dodecyl benzyl, trimethyl ammonium chloride, dodecylbenzene sulfonates, metal and ammonium fatty acid soaps, dodecyl sodium sulfate, dodecyl ammonium sulfate, dodecyl triethanolamine sulfate, myristyl sodium sulfate, myristyl ammonium sulfate, myristyl triethanolamine sulfate, palmityl sodium sulfate, palmityl ammonium sulfate, palmityl triethanolamine sulfate, stearyl sodium sulfate, stearyl ammonium sulfate, stearyl triethanolamine sulfate, and lauryl, myristyl, palmityl and stearyl polyethoxy sodium sulfates wherein ethoxy is 1 to 6 units; and a germicidally effective amount of a quaternary ammonium complex of the formula:



wherein R is selected from the group consisting of alkyl of 8-24 carbon atoms, dodecylbenzyl, octyl phenoxy ethoxy ethyl; wherein R₁ alone is selected from the group consisting of alkyl, phenyl, chlorophenyl, bromophenyl, alkyl-

phenyl, benzyl, alkylbenzyl, dialkylbenzyl, chlorobenzyl, dichlorobenzyl, dibromobenzyl, naphthyl-lower alkyl and alkyl naphthyl ammonium chloride wherein the alkyl is from 8-24 carbon atoms; wherein R₂ alone is lower alkyl; wherein R₃ alone is lower alkyl; wherein R₁ together with one of the groups R₂ and R₃ is selected from the group consisting of morpholino, methylmorpholino and piperidino, and wherein R₁, R₂ and R₃ together is selected from the group consisting of pyridino quinolino and isoquinolino; wherein A, B, D and F are each selected from the group consisting of hydrogen, lower alkyl, chlorine, bromine, iodine, phenyl, lower alkyl phenyl, lower alkoxy phenyl, chlorophenyl, bromophenyl, benzyl, lower alkyl benzyl, lower alkoxy benzyl chlorobenzyl and bromobenzyl; wherein G is selected from the group consisting of lower alkyl, chlorine, bromine, iodine, phenyl, lower alkyl phenyl, lower alkoxy phenyl, chlorophenyl, bromophenyl, benzyl, lower alkyl benzyl, lower alkoxy benzyl, chlorobenzyl and bromobenzyl; wherein Y is selected from the group consisting of oxygen and sulfur; and wherein X is selected from the group consisting of chlorine, bromine and iodine.

2. Detergent germicidal composition according to claim 1 wherein said quaternary ammonium complex is para-octyl phenoxy ethoxy ethyl dimethyl benzyl ammonium ortho phenyl phenate bromine complex.

3. Detergent germicidal composition according to claim 1 wherein said quaternary ammonium complex is alkyl (C₈-C₁₈) dimethyl benzyl ammonium orthophenyl phenate bromine complex.

4. Detergent germicidal composition according to claim 1 wherein said quaternary ammonium complex is dodecyl benzyl trimethyl ammonium ortho-phenyl phenate iodine complex.

5. Detergent germicidal composition according to claim 1 wherein said quaternary ammonium complex is dodecyl trimethyl ammonium ortho-phenyl phenate chlorine complex.

6. Detergent germicidal composition according to claim 1 wherein said quaternary ammonium complex is alkyl (C₈-C₁₈) dimethyl benzyl ammonium cresylate bromine complex.

7. Detergent germicidal composition according to claim 1 wherein said quaternary ammonium complex is alkyl (C₈-C₁₈) dimethyl benzyl ammonium benzyl phenate bromine complex.

8. Detergent germicidal composition according to claim 1 wherein said quaternary ammonium complex is dodecyl benzyl trimethyl ammonium para-phenyl phenate iodine complex.

9. Detergent germicidal composition according to claim 1 wherein said quaternary ammonium complex is alkyl (C₈-C₁₈) dimethyl naphthyl methyl ammonium chlorophenate bromine complex.

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