

UNITED STATES PATENT OFFICE

2,087,131

QUATERNARY AMMONIUM COMPOUNDS

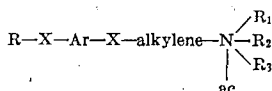
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15 Claims. (Cl. 260—127)

This invention relates to quaternary ammonium compounds which exert a dispersing, disinfecting and preserving action.

In accordance with the present invention new products which are distinguished by a dispersing, disinfecting and preserving action are obtainable by the manufacture of quaternary ammonium compounds of the formula:

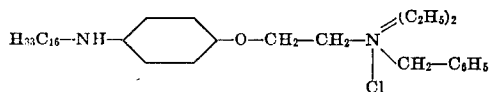


in which formula R, R₁ and R₂ stand for hydrocarbon radicals, R₃ stands for an alkenyl, alkoxyalkyl or phenalkyl group, X stands for one of the members —O—, —S—, —NH— or N—alkyl, Ar stands for an at most bicyclic aromatic ring system and ac stands for an acid radical, such as the radicals of the hydrohalic acids, sulfuric acid, methyl or ethyl sulfuric acid, etc. Accordingly, the said new products are aromatic compounds which contain attached to the aromatic nucleus by an oxygen, sulfur or nitrogen atom a quaternary aminoalkyl group, on the one hand, and, again attached to the nucleus by an oxygen, sulfur or nitrogen atom, a hydrocarbon radical, such as alkyl, cycloalkyl, arylalkyl or aryl groups, on the other hand.

The new products are in part viscous, thickly liquid, in part solid crystalline substances. They dissolve readily in water and form stable aqueous solutions. In view of their dispersing and disinfecting properties they exert a remarkable action as wetting, emulsifying and foaming agents and also as antiseptics and preserving media. Particularly those compounds distinguish by the said properties which contain attached to the aromatic nucleus by oxygen, sulfur or nitrogen a higher alkyl group, such as the butyl, octyl, cetyl group, etc.

The disinfecting and preserving properties of the above characterized group of new quaternary ammonium compounds will become more obvious by stating by way of example the activity of a number of the new compounds against certain bacteria:

N-diethyl-N-benzyl-N-(para-cetylaminophenoxyethyl)-ammonium chloride of the formula:



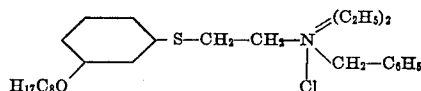
kills in an aqueous solution at room temperature

typhus bacteria in the concentration 1:1000 after 5 minutes, para-typhus B bacteria in the concentration 1:1000 after 10 minutes, dysentery bacteria in the concentration 1:500 after 1 minute, coli bacteria in the concentration 1:250 after 2½ minutes, staphylococci in the concentration 1:1000 after 2½ minutes;

N-diethyl-N-benzyl-N-(3-butyloxyphenoxyethyl)-ammonium chloride kills coli bacteria in the concentration 1:500 after 2½ minutes, staphylococci in the concentration 1:5000 after 2½ minutes;

N-diethyl-N-benzyl-N-(3-n-octyloxyphenoxyethyl)-ammonium chloride kills coli bacteria in the concentration 1:10000 after 2½ minutes, staphylococci in the concentration 1:25000 after 2½ minutes;

N-diethyl-N-benzyl-N-(n-octyloxyphenylthioethyl)-ammonium chloride of the formula:



kills coli bacteria in the concentration 1:10000 after 2½ minutes, staphylococci in the concentration 1:25000 after 2½ minutes;

N-diethyl-N-benzyl-N-(3-octylthiophenoxyethyl)-ammonium chloride kills coli bacteria in the concentration 1:10000 after 2½ minutes, staphylococci in the concentration 1:50000 after 2½ minutes;

N-diethyl-N-benzyl-N-(3-butylamino-4-cresyloxyethyl)-ammonium chloride kills coli bacteria in the concentration 1:5000 after 2½ minutes, staphylococci in the concentration 1:50000 after 2½ minutes.

The presence of a bactericidal and fungicidal action in combination with a more or less foaming and purifying action and the fact that the new products are odorless and relatively non-toxic for man, render the new compounds generally useful disinfectants and cleansing agents. They are particularly suitable for the disinfection and cleaning of eating, drinking and storage utensils. They are further advantageously used for the cleaning and disinfection of medical instruments and other commodities, laundry, etc. Furthermore, floors and walls may be cleaned and disinfected by the new substances. The new products may be further used for the cleaning, disinfection and preservation of food, such as meat, vegetables, fruits, and animal material, such as hides and skins, glands, and similar animal organs.

The new products may also be used in dilution with very hard water without diminution of their activity. In the concentrations required for the disinfection and purification processes they do not injure the human skin and may therefore be used also for disinfecting the skin, particularly the hands.

The new products may be used in substance as well as in solution or emulsion and if desired in admixture with each other and/or with other active or inert substances, such as powder, ointment bases, creams and the like.

In accordance with the present invention the new quaternary ammonium compounds are obtainable by reacting upon an aromatic compound which contains attached to the aromatic nucleus by an oxygen, sulfur or nitrogen atom a tertiary aminoalkyl group, on the one hand, and contains attached to the nucleus by oxygen, sulfur or nitrogen a saturated or unsaturated alkyl or cycloalkyl, arylalkyl or aryl radical, on the other hand, with an ester of an unsaturated, an alkoxy- or phenyl-substituted alcohol. Such unsaturated alkyl, alkoxyalkyl or phenalkyl esters are, for instance, the esters of unsaturated or of alkyl- or phenyl-substituted alcohols with mineral acids, such as halohydric acids, sulfuric acid or substitution products of the sulfuric acid, such as aryl and alkyl sulfuric acids, for instance, dimethyl- and diethyl-sulfate, benzene and toluene sulfonic acid alkyl esters. These esters may also first serve for the transformation of compounds of the kind specified, however, containing the aliphatically bound amino group in the primary or secondary state, into the corresponding tertiary compounds and then further converting the tertiary compounds into the quaternary compounds in the manner set forth above.

In further development of the present invention it has been found that the new quaternary compounds are also obtainable by reacting upon an aromatic compound which contains attached to the nucleus by oxygen, sulfur or nitrogen a saturated or unsaturated alkyl, cycloalkyl, aralkyl or aryl radical, on the one hand, and again attached to the nucleus by oxygen, sulfur and nitrogen an aliphatic radical substituted by a replaceable substituent, such as halogen atoms or ester-like bound radicals of the sulfuric or alkyl- or aryl sulfuric acids, on the other hand, with a tertiary amine.

The new products are further obtainable by reacting upon an aromatic compound containing a primary amino group attached to the nucleus, on the one hand, and containing attached to the nucleus by oxygen, sulfur or nitrogen a quaternary aminoalkyl group, on the other hand, with an ester of a saturated or unsaturated aliphatic or cyclic alcohol or arylalcohol, for instance, an ester of the said alcohols with a hydrohalic acid or with sulfuric acid. The said process may be modified in such a way that an aromatic primary amine the aliphatically bound amino group of which is not yet present in its quaternary state is used as starting material and that by the action of the said esters of saturated or unsaturated alcohols or arylalcohols the aliphatically bound amino group is converted into its quaternary state and the aromatically bound amino group is substituted by the saturated or unsaturated alkyl, cycloalkyl or arylalkyl radical.

The compounds used in the said processes as starting materials may contain beside the characteristic groups specified other substituents which do not prevent the reaction, such as

halogen, hydroxyl, saturated or unsaturated alkyl or cycloalkyl, nitro, sulfo, cyano or carboxyl groups.

The invention is further illustrated by the following examples without being restricted thereto:

(1) 225 parts by weight of 3-methoxyphenyl-beta-diethylaminoethylether, obtainable by treatment of sodium 3-methoxyphenolate with diethylaminoethylchloride as a colorless liquid boiling at 144-147° C. under 6 mm. pressure, are treated with 127 parts by weight of benzylchloride. The mixture is heated in a pressure vessel to 100° C. for 24 hours. The N-diethyl-N-benzyl-3-methoxyphenoxyethylammonium chloride thus obtained after cooling is a viscous, yellowish brown, transparent mass, which clearly dissolves in water and alcohol.

The quaternary salt is further obtained by heating molecular quantities of 3-methoxyphenyl-beta-diethylaminoethylether and benzylchloride for about 3 hours with the six- to nine-fold quantity of distilled water. Likewise, alcohol and benzene may be used as diluents. Further, the new compound may be obtained by heating the components for 1 to 2 days without the employment of pressure vessels.

In an analogous manner either by direct reaction of the components in molecular proportions, if desired, also with the addition of indifferent solvents or diluents, as, for instance, benzene or alcohol, the following quaternary compounds are obtained in the form of viscous, transparent masses which, on longer storage or on rubbing on with cyclohexane, become crystalline.

(2) N-diethyl-N-benzyl-3-butyloxyphenoxyethylammonium chloride from benzylchloride and 3-butyloxy phenyl-beta-diethylaminoethylether (obtainable by treatment of sodium 3-butyloxyphenolate with diethylaminoethyl chloride as a yellowish oil boiling at 165-167° C. under 2 mm. pressure).

(3) N-diethyl-N-benzyl-3-cyclohexyloxyphenoxyethylammonium chloride from benzylchloride and 3-cyclohexyloxyphenoxyethylammonium chloride from benzylchloride and 3-cyclohexyloxyphenyl-beta-diethylaminoethylether (obtainable by treatment of sodium 3-cyclohexyloxyphenolate with diethylaminoethylchloride as a viscous, yellowish oil boiling at 185-190° C. under 1 mm. pressure).

(4) N-diethyl-N-benzyl-3-n-octyloxyphenoxyethylammonium chloride from benzylchloride and 3-n-octyloxyphenyl-beta-diethylaminoethylether (obtainable by treatment of sodium 3-n-octyloxyphenolate with diethylaminoethylchloride as a pale yellow oil boiling at 190-192° C. under 1 mm. pressure).

(5) N-diethyl-N-allyl-3-n-octyloxyphenoxyethylammonium bromide from allylbromide and 3-n-octyloxyphenyl-beta-diethylaminoethylether.

(6) N-diethyl-N-benzyl-2-n-octyloxyphenoxyethylammonium chloride from benzylchloride and 2-n-octyloxyphenyl-beta-diethylaminoethylether (obtainable by treatment of sodium 2-n-octyloxyphenolate with diethylaminoethylchloride as a colorless oil boiling at 195-198° C. under 5 mm. pressure).

(7) N-diethyl-N-benzyl-4-n-octyloxyphenoxyethylammonium chloride from benzylchloride and 4-n-octyloxyphenyl-beta-diethylaminoethylether (obtainable by treatment of sodium 4-n-octyloxyphenolate with diethylaminoethylchloride as a colorless oil boiling at 203-205° C. under 4 mm. pressure).

(8) N-diethyl-N-benzyl-3-dodecyloxyphenoxyethylammonium chloride from benzylchloride and 3-dodecyloxyphenyl-beta-diethylaminoethylether (obtainable by treatment of sodium 3-dodecyloxyphenolate with diethylaminoethylchloride as a yellowish colored oil boiling at 212-213° C. under 2 mm. pressure).

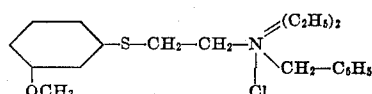
(9) N-diethyl-N-benzyl-3-benzyloxyphenoxyethylammonium chloride from benzylchloride and 3-benzyloxyphenyl-beta-diethylaminoethylether (obtainable by treatment of sodium 3-benzyloxyphenolate with diethylaminoethylchloride as a yellowish oil boiling at 212-215° C. under 1 mm. pressure).

(10) N-diethyl-N-benzyl-3-ortho-chlorobenzyloxyphenoxyethylammonium chloride from benzylchloride and 3-ortho-chlorobenzyloxyphenyl-beta-diethylaminoethylether (obtainable by treatment of sodium 3-ortho-chlorobenzyloxyphenolate with diethylaminoethylchloride as a yellowish oil boiling at 201-203° C. under 1 mm. pressure).

(11) N-diethyl-N-benzyl-3-benzyloxychlorophenoxyethylammonium chloride from benzylchloride and 3-benzyloxychlorophenyl-beta-diethylaminoethylether (obtainable by treatment of sodium 3-benzyloxychlorophenolate with diethylaminoethylchloride as a yellowish oil boiling at 197-200° C. under 0.5 mm. pressure).

(12) N-diethyl-N-benzyl-2-methoxy-6-allylphenoxyethylammonium chloride from benzylchloride and 2-methoxy-6-allylphenyl-beta-diethylaminoethylether.

(13) N-diethyl-N-benzyl-3-methoxyphenylthioethylammonium chloride of the formula



from benzylchloride and 3-methoxyphenyl-beta-diethylaminoethylthioether (obtainable by treatment of sodium 3-methoxythiophenolate with diethylaminoethylchloride as a colorless oil boiling at 156-158° C. under 3 mm. pressure).

(14) N-benzyl-N-diethyl-3-methoxyphenylthioethylammoniumiodide, from benzyl iodide and 3-methoxyphenyl-beta-diethylaminoethylthioether.

(15) N-diethyl-N-benzyl-3-n-octyloxyphenylthioethylammoniumchloride from benzylchloride and 3-n-octyloxyphenyl-beta-diethylaminoethylthioether (obtainable by treatment of sodium 3-diethylaminoethylthiophenolate with n-octylbromide as a yellowish oil boiling at 190-195° C. under 1 mm. pressure).

(16) N-diethyl-N-benzyl-3-octylthiophenoxyethylammoniumchloride from benzylchloride and 3-octylthiophenyl-beta-diethylaminoethylether (obtainable by treatment of sodium 3-diethylaminoethoxythiophenolate with n-octylbromide as a yellow oil boiling at 198-203° C. under 1 mm. pressure).

(17) N-diethyl-N-benzyl-3-butylaminophe-noxyethylammoniumchloride from benzylchloride and 3-butylaminophenyl-beta-diethylaminoethylether (obtainable by treatment of sodium 3-butylaminophenolate with diethylaminoethylchloride as a yellow oil boiling at 175-177° C. under 1 mm. pressure).

(18) N-diethyl-N-benzyl-3-butylamino-para-cresoxyethylammoniumchloride from benzylchloride and 3-butylamino-4-cresyl-beta-diethylaminoethylether, obtainable by treatment of sodium 3-butylamino-para-cresolate with dieth-

ylaminoethylchloride as a yellow oil boiling at 176-178° C. under 3 mm. pressure.

(19) N-benzyl-N-diethyl-3-butylamino-4-cresoxyethylammoniumiodide from benzyl iodide and 3-butylamino-4-cresyl-beta-diethylaminoethylether.

(20) N-diethyl-N-benzyl-3-n-octyloxyphenylaminoethylammoniumchloride from benzylchloride and N-3-octyloxyphenyl-beta-diethylaminoethylamine (obtainable by treatment of 3-n-octyloxyphenylamine with diethylaminoethylchloride as a yellow oil boiling at 215-220° C. under 3 mm. pressure).

(21) N-diethyl-N-benzyl-3-n-octylaminophe-noxyethylammoniumchloride from benzylchloride and 3-n-octylaminophenyl-beta-diethylaminoethylether (obtainable by treatment of sodium 3-n-octylaminophenolate with diethylaminoethylchloride as a viscous oil boiling at 195-200° C. under 1 mm. pressure).

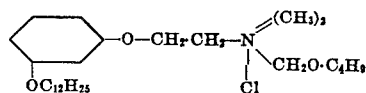
(22) N-diethyl-N-benzyl-1-hexylamino-3-naphthyl-oxyethylammoniumchloride from benzylchloride and 1-hexylamino-3-naphthyl-beta-diethylaminoethylether (obtainable by treatment of 1-amino-3-diethylaminoethoxynaphthalene with n-hexylbromide as a viscous oil boiling at 233-236° C. under 2 mm. pressure).

(23) N-diethyl-N-benzyl-1-n-octylamino-3-naphthyl-oxyethylammoniumchloride from benzylchloride and 1-n-octylamino-3-naphthyl-beta-diethylaminoethylether (obtainable by treatment of 1-amino-3-diethylaminoethoxynaphthalene with n-octylbromide as a viscous oil boiling at 238-240° C. under 0.15 mm. pressure).

(24) N-diethyl-N-benzyl-para-phenoxyphenylaminoethylammoniumchloride from benzylchloride and para-phenoxydiethylaminoethylaniline (obtainable by treatment of para-phenoxyphenylamine with diethylaminoethylchloride boiling at 196-200° C. under 2 mm. pressure).

(25) N-diethyl-N-dodecyloxymethyl-3-methoxyphenoxyethylammoniumchloride which already is obtained by triturating dodecyloxymethylchloride with 3-methoxyphenyl-beta-diethylaminoethylether.

(26) N-dimethyl-N-butyloxymethyl-3-dodecyloxyphenoxyethylammoniumchloride of the formula:



by rubbing butyloxymethylchloride with 3-dodecyloxyphenyl-beta-dimethylaminoethylether (obtainable by treatment of sodium 3-dodecyloxyphenolate with dimethylaminoethylchloride as a yellow oil boiling at 200-205° C. under 2 mm. pressure).

(27) N-dimethyl-N-benzyl-alpha-(3-n-octyloxyphenoxy)-beta-hydroxypropylammoniumchloride from benzylchloride and N-dimethyl-alpha-(3-n-octyloxyphenoxy)-beta-hydroxypropylamine (obtainable by reacting upon sodium 3-n-octyloxyphenolate with gamma-dimethylamino-beta-hydroxy-propylchloride as a yellowish oil boiling at 205-208° C. under 1 mm. pressure).

(28) N-dimethyl-N-benzyl-gamma-(3-n-hexyloxyphenoxy)-propylammoniumchloride from benzylchloride and 3-n-hexyloxyphenyl-gamma-dimethylaminopropylether (obtainable by reacting upon sodium 3-n-hexyloxyphenolate with gamma-dimethylaminopropylchloride as a

yellowish oil boiling at 198–201° C. under 1 mm. pressure).

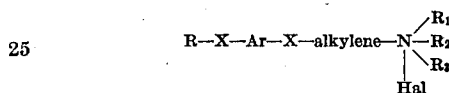
(29) N-diethyl-N-para-nitrobenzyl-3-N-octyloxy-phenoxy ethylammoniumchloride from para-nitrobenzylchloride and 3-n-octyloxyphenyl-beta-diethylaminoethylether.

(30) N-dimethyl-N-phenylethyl-gamma-(3-butyloxyphenoxy)-beta-dimethylpropylammoniumbromide from phenylethylbromide and N-dimethyl-gamma-3-butyloxyphenoxy)-beta-dimethylpropylamine (obtainable by reacting upon sodium-3-butyloxyphenolate and gamma-dimethylamino-beta-dimethylpropylchloride as an oil burning at 195–200° C. under 1 mm. pressure).

(31) N-diethyl-N-hydroxyphenylpropyl-N-(3-octyloxyphenoxyethyl)-ammoniumbromide from hydroxyphenylpropylbromide and N-diethyl-3-octyloxyphenoxyethylamine (obtainable by reacting upon sodium 3-octyloxyphenolate with diethylaminoethylchloride).

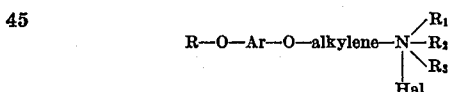
We claim:—

1. The products of the formula:



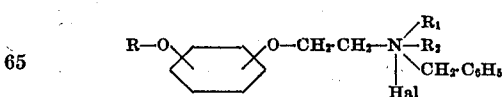
in which R stands for a radical selected from the group consisting of alkyl, cyclohexyl, phenyl, and phenylalkyl and halogen-phenylalkyl of the lower aliphatic series, R₁ and R₂ stand for the same lower alkyl groups, R₃ stands for a radical selected from the group consisting of alkenyl of the type of allyl and of alkoxy- and phenyl-substituted lower alkyl groups, X stands for one of the members —O— and —S—, Ar stands for an aromatic radical selected from the group consisting of radicals of the benzene and naphthalene series, "alkylene" is of the lower aliphatic series, and Hal stands for a halogen atom, which products are soluble in water and have a disinfecting, preserving and dispersing power.

2. The products of the formula:



in which R stands for a radical selected from the group consisting of alkyl, cyclohexyl, phenyl, and phenylalkyl and halogen-phenylalkyl of the lower aliphatic series, R₁ and R₂ stand for the same lower alkyl groups, R₃ stands for a radical selected from the group consisting of alkenyl of the type of allyl and of alkoxy- and phenyl-substituted lower alkyl groups, Ar stands for a benzene radical, "alkylene" is of the lower aliphatic series, and Hal stands for a halogen atom, which products are soluble in water and have a disinfecting, preserving and dispersing power.

3. The products of the formula:



in which R stands for a radical selected from the group consisting of alkyl, cyclohexyl, phenyl, and phenylalkyl and halogen-phenylalkyl of the lower aliphatic series, R₁ and R₂ stand for the same lower alkyl groups, and Hal stands for a halogen atom, which products are soluble in water and have a disinfecting, preserving and dispersing power.

4. The process which comprises reacting upon a compound of the formula:



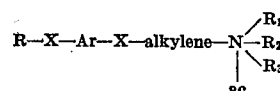
wherein Ar stands for a benzene radical, "(alkyl)₂" and "alkylene" are of the lower aliphatic series, and X stands for one of the members —O— and —S—, with a benzylhalide.

5. The process which comprises reacting upon a compound of the formula:



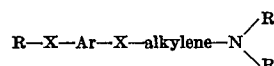
wherein Ar stands for a benzene radical, "(alkyl)₂" and "alkylene" are of the lower aliphatic series, with a benzylhalide.

6. The products of the formula:



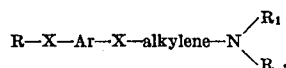
in which R stands for a radical selected from the group consisting of alkyl, cyclohexyl, phenyl, and phenylalkyl and halogen-phenylalkyl of the lower aliphatic series, R₁ and R₂ stand for the same lower alkyl groups, R₃ stands for a radical selected from the group consisting of alkenyl of the type of allyl and of alkoxy- and phenyl-substituted lower alkyl groups, X stands for one of the members —O— and —S—, Ar stands for an aromatic radical selected from the group consisting of radicals of the benzene and naphthalene series, "alkylene" is of the lower aliphatic series, and ac stands for the anion of an inorganic acid radical, which products are soluble in water and have a disinfecting, preserving and dispersing power.

7. The process which comprises reacting upon a compound of the formula:



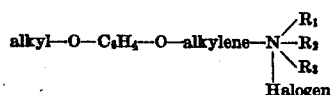
in which R stands for a radical selected from the group consisting of alkyl, cyclohexyl, phenyl and phenylalkyl and halogen-phenylalkyl of the lower aliphatic series, R₁ and R₂ stand for the same lower alkyl groups, X stands for one of the members —O— and —S—, "alkylene" is of the lower aliphatic series, and Ar stands for an aromatic radical selected from the group consisting of radicals of the benzene and naphthalene series, with a reactive inorganic acid ester selected from the group consisting of inorganic acid esters of alkoxy-substituted and phenyl-substituted lower alkyl monohydric alcohols.

8. The process which comprises reacting upon a compound of the formula:



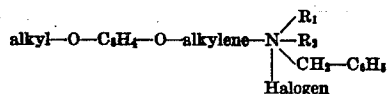
in which R stands for a radical selected from the group consisting of alkyl, cyclohexyl, phenyl and phenylalkyl and halogen-phenylalkyl of the lower aliphatic series, R₁ and R₂ stand for the same lower alkyl groups, X stands for one of the members —O— and —S—, "alkylene" is of the lower aliphatic series, and Ar stands for an aromatic radical selected from the group consisting of radicals of the benzene and naphthalene series, with a hydrohalic acid ester of a phenyl-substituted lower alkyl monohydric alcohol.

9. The products of the formula:



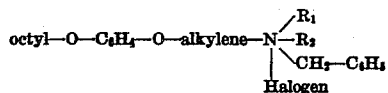
in which "alkylene" is of the lower aliphatic series, R_1 and R_2 stand for the same lower alkyl groups, R_3 stands for a radical selected from the group consisting of alkenyl of the type of allyl and of alkoxy- and phenyl-substituted lower alkyl groups, which products are soluble in water and have a disinfecting, preserving and dispersing power.

10. The products of the formula:



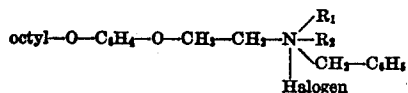
in which "alkylene" is of the lower aliphatic series, and R_1 and R_2 stand for the same lower alkyl groups, which products are soluble in water and have a disinfecting, preserving and dispersing power.

11. The products of the formula:



in which "alkylene" is of the lower aliphatic series, and R_1 and R_2 stand for the same lower alkyl groups, which products are soluble in water and have a disinfecting, preserving and dispersing power.

12. The products of the formula:



in which R_1 and R_2 stand for the same lower alkyl groups, which products are soluble in water and have a disinfecting, preserving and dispersing power.

13. N-diethyl-N-benzyl-3-n-octyloxyphenoxyethylammonium-chloride, which product is soluble in water and has a disinfecting, preserving and dispersing power.

14. N-diethyl-N-benzyl-3-n-dodecyloxyphenoxyethylammonium-bromide, which product is soluble in water and has a disinfecting, preserving and dispersing power.

15. N-diethyl-N-benzyl-4-n-octyloxyphenoxyethylammonium-chloride, which product is soluble in water and has a disinfecting, preserving and dispersing power.

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