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3,539,684
BACTERICIDAL POLYMERS
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Int. Cl. A01n 23/00, 9/22
U.S. Cl. 424—78

9 Claims

ABSTRACT OF THE DISCLOSURE

Bactericidal effects of various homopolymers and copolymers of fatty quaternary diallyl ammonium compounds are disclosed.

BACKGROUND OF THE INVENTION

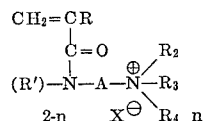
It has been known for years that certain quaternary ammonium compounds are excellent bactericides. Although it is very common for quaternary ammonium compounds to have bactericidal effects, it is also known that not all quaternary ammonium compounds display such abilities. It nevertheless may be said that, generally speaking, quaternary ammonium compounds having fatty tails exhibit excellent bactericidal and bacteristatic effects. See, for example, "Surface Active Quaternary Ammonium Germicides" by Carl Lawrence, Academic Press, Inc., 1950.

Attempts have been made to incorporate fatty quaternary ammonium groups into polymers, generally water soluble polymers. However, little success has been achieved. See also, for example, Melamed, U.S. Pats. 2,980,634 and 2,980,657. Other examples can be found in British Pat. 1,059,117 and U.S. Pat. 2,309,592. I have found that fatty quaternary ammonium groups may be incorporated into long chain water-soluble polymers when they are generally of the structure disclosed by Butler in U.S. Pat. 3,288,770. See my patent application filed Dec. 15, 1967, Ser. No. 690,793 now abandoned.

SUMMARY OF THE INVENTION

I have found that water soluble polymers containing at least 0.5% by weight of a fatty alkyl diallyl quaternary ammonium compound exhibit excellent bacteristatic and bactericidal properties. The balance of the polymers of my invention may be comprised of other diallyl quaternary ammonium monomers and/or monoethylenically unsaturated monomers.

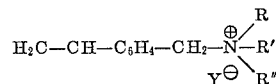
Examples of the copolymerizable monoethylenically unsaturated comonomers are acrylamide and the N-substituted acrylamides disclosed in British Pat. 788,079. Examples are N-(2-diethylamino-ethyl)-methacrylamide, N-(3-dimethylamino-propyl)-methacrylamide, N-(2-piperidino-ethyl)-methacrylamide, N-(2-dimethylamino-ethyl)-acrylamide, N-(2-diethylaminoethyl)-acrylamide, and N-(3-dimethylamino-propyl)-acrylamide, N-(2-morpholinethyl)-methacrylamide, N-(3-piperidino-propyl)-methacrylamide and N-(3-hexamethylene-aminopropyl)-methacrylamide. Included in this group are monomers disclosed in U.S. Pat. 2,980,657, namely those of the formula



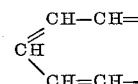
where R is hydrogen or methyl, R' is independently hydrogen or a lower alkyl group having 0 to 4 carbon atoms, A is a straight or branched chain alkylene group having 2 to 10 carbon atoms or a divalent saturated aliphatic group

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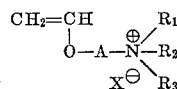
consisting of a plurality of alkylene groups of 2 to 10 carbon atoms each pair of which is connected by an ether oxygen atom, R₂ and R₃ may be (1) separate groups selected individually from the group consisting of alkyl groups having 1 to 12 carbon atoms, hydroxyalkyl groups having 2 to 12 carbon atoms, alkoxyalkyl groups having 2 to 12 carbon atoms, and (2) a single saturated aliphatic group which together with the N atom forms a heterocyclic group containing 5 to 6 atoms in the ring of which 4 to 5 are carbon and which may contain a second atom of the group consisting of O, N, and S, the second atom, if nitrogen, being substituted by an alkyl group having 1 to 18 carbon atoms, R₄ is selected from saturated and unsaturated aliphatic hydrocarbon groups having 1 to 18 carbon atoms (polyalkoxy) alkyl groups having 2 to 18 carbon atoms, hydroxyalkyl groups having 2 to 18 carbon atoms, an aralkyl or substituted aralkyl group having 7 to 24 carbon atoms, or a phenoxyalkyl group having 7 to 24 carbon atoms, X is OH or a negative, salt-forming atom or radical, and n is an integer having a value from 1 to 2. The N-3-oxohydrocarbon-substituted acrylamides, such as diacetone acrylamide, disclosed in U.S. Pat. 3,277,056, are also useful; other useful monomers include vinyl benzyl monomers of the general formula



wherein R, R' and R'' each represents individually a monovalent radical selected from the group consisting of CH₂OHCH₂—; CH₃CHOHCH₂—; CH₂OHCHOHCH₂—; and alkyl of 1 to 4 carbon atoms, aryl, cycloalkyl, and arylalkyl hydrocarbon radicals, and R, R' and R'' collectively represent the trivalent radical of the formula



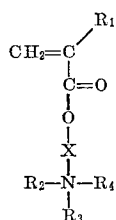
wherein, the three valences are attached to the nitrogen atom, and said R groups containing a total of not more than 12 carbon atoms in the sum of the constituent radicals, and Y is an anion, such as are discussed in Silvernail and Zembal U.S. Pat. 3,011,918. Also included are monomers disclosed in U.S. Pat. 2,980,634 having the formula



in which A is ethylene, trimethylene, or —CHR—CH₂— where R may be any alkyl or alkenyl group having from 1 to 16 carbon atoms, R₁ and R₂ may be (1) separate groups selected individually from the group consisting of alkyl or alkenyl groups having 1 to 12 carbon atoms, hydroxyalkyl groups having 2 to 12 carbon atoms, polyalkoxy-alkyl groups having 2 to 12 carbon atoms, or (2) R₁ and R₂ may together represent the morpholino residue: (C₂H₄)₂O, the pyrrolidino residue, —C₄H₈—, the piperidino residue, —C₅H₁₀—, and an N-alkyl-piperazine residue: (C₂H₄)₂:NR⁰ where R⁰ is an alkyl of 1 to 18 carbon atoms, such as methyl, ethyl, isopropyl, R₃ is selected from saturated and ethylenically unsaturated aliphatic hydrocarbon groups having 1 to 18 carbon atoms (polyalkoxy) alkyl groups having 2 to 18 carbon atoms, alkoxyalkyl groups having 2 to 18 carbon atoms, hydroxyalkyl groups having 2 to 18 carbon atoms, and aralkyl or substituted aralkyl groups having 7 to 24 carbon atoms, or a phenoxyalkyl group having 7 to 24 carbon atoms, at least one of R₁, R₂ and R₃ has at least 7 carbon atoms, and X is OH or a negative, salt-forming atom or radical preferably of monovalent character, such

as halide, e.g., bromide, chloride, iodide, sulfate, e.g., the methyl sulfate anion, and sulfonate, e.g., p-toluene- or cyclohexyl-sulfonate anions.

In addition, monomers may be used such as are disclosed and discussed in Hayek U.S. Pat. 2,741,568, of the general formula



where R_1 is a member of the class consisting of hydrogen, methyl and ethyl radicals, R_2 , R_3 and R_4 are alkyl radicals of from 1 to 4 carbon atoms, and X is a saturated bivalent hydrocarbon radical of from 1 to 4 carbon atoms, or a bivalent hydroxyalkyl radical of 1 to 4 carbon atoms (see Formula IV in U.S. Pat. 2,810,713).

Examples of the diallyl quaternary ammonium comonomers are dimethyl diallyl ammonium chloride, diethyl diallyl ammonium chloride and methyl β -propionamido diallyl ammonium chloride. For other examples see Butler U.S. Pat. 3,288,770.

The preferred polymers of my invention are copolymers of at least 0.5% by weight of a fatty quaternary diallyl ammonium chloride and the remainder dimethyl diallyl ammonium chloride and/or acrylamide.

Surprisingly enough, I have found that the fatty quaternary diallyl ammonium monomers exhibit no significant bactericidal or bacteriostatic properties. Only when water soluble polymers are prepared having at least 0.5% by weight of a fatty quaternary diallyl ammonium group is an operable composition achieved.

The following Table I illustrates the effects of my polymer compositions on *Aerobacter aerogenes*. The results shown were for a time kill test. All compositions are reported on a percent by weight basis. A description of a time kill test is as follows:

TIME KILL TEST

(1) A stock bacteria solution was prepared in the following manner. A beef extract nutrient broth (Official Methods of Analyses of the Association of Official Agricultural Chemists, Tenth edition, 1965, page 80, Reagent (a)) was inoculated with *Aerobacter aerogenes* and incubated for 24 hours at 35° C. Ten milliliters of the broth was then added to 90 milliliters of sterilized deionized water.

(2) Stock solutions of the compound to be tested were prepared such that 1 milliliter contained the desired p.p.m. of active compound.

(3) One milliliter of the stock bacteria solution and 1 milliliter of the stock compound solution were added to 48 milliliters of sterilized deionized water. The solution was left standing for a contact time for 3 hours.

(4) After 3 hours of contact time, 1 milliliter was withdrawn and appropriate serial dilutions performed in sterile phosphate buffered (KH_2PO_4) deionized water. Then 1 milliliter of this diluted solution was plated in Trypton glucose extract agar and incubated for 24 hours at 35° C.

(5) After incubation the plates were counted and the percent reduction (kill) calculated using a control count as reference. The control was prepared in the same manner except the compound solution was not added and the contact time was 0 hours.

TABLE I

Formulation	Test, p.p.m.	Percent kill
1. Homopolymer of MODAAC.....	1 10	100 100
2. Homopolymer of MDDAAC.....	1 10	100 100
3. Copolymer of 5% MODAAC, 95% of DMDAAC.....	1 10	100 100
4. Copolymer of 75% MODAAC, 25% DMDAAC.....	1 10	100 100
5. Copolymer of 5% MDDAAC, 95% DMDAAC.....	1 10	100 100
6. Copolymer of 50% MDDAAC, 50% DMDAAC.....	1 10	100 100
7. Copolymer of 75% MODAAC, 25% acrylamide.....	1 10	99 99
8. Copolymer of 5% MDDAAC, 95% acrylamide.....	1 10	0 95
9. Copolymer of 75% MDDAAC, 25% DMDAAC.....	1 10	99 99
10. Copolymer of 20% MODAAC, 40% DMDAAC, 40% acrylamide.....	1 10	99 99
11. Copolymer of 20% MDDAAC, 40% DMDAAC, 40% acrylamide.....	1 10	99 99

NOTE.—MODAAC = methyl n-octyl diallyl ammonium chloride; MDDAAC = methyl n-dodecyl diallyl ammonium chloride; DMDAAC = dimethyl diallyl ammonium chloride.

Table II illustrates the effects of the fatty quaternary diallyl ammonium chloride monomers on *Aerobacter aerogenes*. The results shown were for a time kill test.

TABLE II

Monomer	Dosage in p.p.m.	Percent kill
1. Methyl n-octyl diallyl, ammonium chloride.....	1 10	4 10
2. n-Octyl benzyl diallyl, ammonium chloride.....	1 10	0 0
3. Methyl dodecyl diallyl, ammonium chloride.....	1 10	4 51

A contrast of Tables I and II indicates that the fatty diallyl quaternary ammonium monomers are ineffective against bacteria when compared to the polymers containing them.

It is apparent that it would be difficult to ascertain the minimum concentration below which my polymers will have no biocidal effects. However, for all practical purposes it may be assumed that at least about 0.5 part of polymer per million parts of water should be present. As is known in the art of bactericides, there is some minimum contact time below which results are negligible.

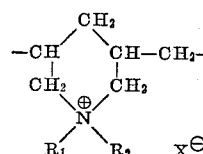
Another factor which should be kept in mind when using the polymers of my invention is that they are highly cationic and will tend to lose their effectiveness in the presence of polyanionic compounds.

The polymers of this invention have utility in treating circulating water systems such as cooling towers and swimming pools to inhibit growth of algae and bacteria. The polymers may also be used to inhibit growth of algae and bacteria in ponds, reservoirs, and other bodies of stagnant water.

I do not intend to be restricted to the above specific examples and illustrations. My invention may be otherwise practiced within the scope of the following claims.

I claim:

1. Method of treating an aqueous medium to inhibit the growth of bacteria therein comprising dissolving in such aqueous medium an effective amount of a random, linear, water soluble polymer consisting essentially of repeating units of the following formula



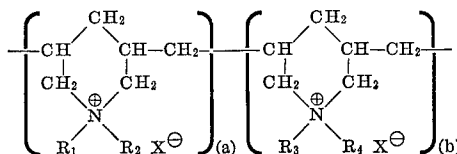
where R_1 is an alkyl group of C_8 to C_{18} ; R_2 is selected from the group consisting of H, alkyl of C_1 to C_{18} , and β -propionamido, and X is an anion selected from the group consisting of F^- , Cl^- , Br^- , I^- , CH_3SO_4^- , and CH_3COO^- .

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2. Method of claim 1 where R_1 is C_8 , R_2 is CH_3 and X is Cl^- .

3. Method of claim 1 where R_1 is C_{12} , R_2 is CH_3 , and X is Cl^- .

4. Method of treating an aqueous medium to inhibit the growth of bacteria therein comprising dissolving in such aqueous medium an effective amount of a random, linear, water soluble polymer of the following formula

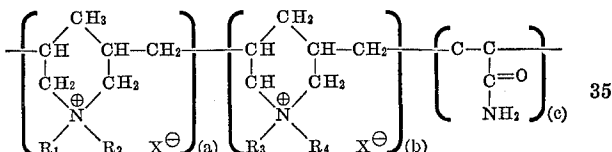


where R_1 is an alkyl group of C_8 to C_{18} ; R_2 is selected from the group consisting of H and alkyl of C_1 to C_{18} ; R_3 is an alkyl group of C_1 to C_4 ; R_4 is selected from the group consisting of H, R_3 , and alkyl group of C_1 to C_4 ; X is an anion independently selected from the group consisting of F^- , Cl^- , Br^- , I^- , $CH_3SO_4^-$ and CH_3COO^- ; a is 0.5% by weight to 97.5% by weight and b is 2.5% to 99.5% by weight.

5. Method of claim 4 where R_1 is C_8 ; R_2 , R_3 , and R_4 are CH_3 and X is Cl^- .

6. Method of claim 4 where R_1 is C_{12} ; R_2 , R_3 , and R_4 are CH_3 and X is Cl^- .

7. Method of treating an aqueous medium to inhibit the growth of bacteria therein comprising dissolving in such aqueous medium an effective amount of a random, linear, water soluble copolymer of the formula



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where R_1 is an alkyl group of C_8 to C_{18} ; R_2 is selected from the group consisting of H and alkyl of C_1 to C_{18} ; R_3 is an alkyl group of C_1 to C_4 ; R_4 is selected from the group consisting of H, R_3 and alkyl group of C_1 to C_4 ; X is an anion independently selected from the group consisting of F^- , Cl^- , Br^- , I^- , $CH_3SO_4^-$, and CH_3COO^- ; a is 0.5% by weight to 97.5% by weight; b is from 0 to 97% by weight; c is from 2.5% to 9.5% by weight.

8. Method of claim 7 where R_1 is C_8 , R_2 , R_3 and R_4 are CH_3 , and X is Cl^- .

9. Method of claim 7 where R_1 is C_{12} , R_2 , R_3 , and R_4 are CH_3 , and X is Cl^- .

References Cited

UNITED STATES PATENTS

2,595,225	5/1952	Coffman	260—88.3
2,923,701	2/1960	Schuller et al.	
2,980,634	4/1961	Melamed.	
2,980,657	4/1961	Melamed.	
3,147,218	9/1964	Booth et al.	210—54
3,288,770	11/1966	Butler.	

FOREIGN PATENTS

1,059,117	2/1967	Great Britain.
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LEWIS GOTTS, Primary Examiner

G. HOLLRAH, Assistant Examiner

U.S. Cl. X.R.

111—67, 85; 260—80.73

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

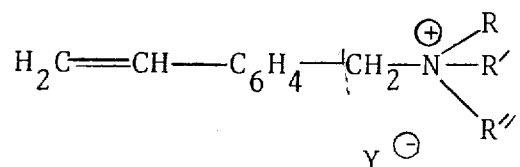
Patent No. 3,539,684

November 10, 1971

Merwin Frederick Hoover

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, lines 25 to 29, the formula should appear as shown below:



same column 2, line 58, "reprsent" should read -- represent --
Column 5, lines 31 to 38, in section B of the formula, the left symbol in the ring structure reading

CH should read CH₂

Column 6, line 7, "9.5%" should read -- 99.5% --.

Signed and sealed this 6th day of April 1971.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

WILLIAM E. SCHUYLER
Commissioner of Patents