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QUATERNARY SALTS OF DIMER ACIDS

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The object of the present invention is the preparation of microbiologically active, relatively water-insoluble compounds by reaction of certain microbiologically active quaternary ammonium hydroxides or their water-soluble salts with dibasic acids obtained by the dimerization of unsaturated fatty acids containing eighteen carbon atoms.

Typical examples of the quaternary ammonium compounds which may be used in this invention are the alkyl trimethyl ammonium chlorides, alkyl benzyl trimethyl ammonium chlorides, alkyl dimethyl benzyl ammonium chlorides, alkyl dimethyl menaphthyl ammonium chlorides, alkyl dimethyl substituted benzyl ammonium chlorides in which the benzyl radical is substituted with one or more side chains containing from 1 to 4 carbon atoms such, for example, as methyl, dimethyl, ethyl and the like and in which the carbon atoms may all be in the same or different side chains or in which the benzyl radical bears one, two or more halogen atoms such as chlorine or bromine, alkyl pyridinium chlorides, alkyl isoquinolinium chlorides and bromides, alkyl lower-alkyl pyrrolidinium chlorides, alkyl lower-alkyl morpholinium chlorides in all of which the alkyl group may have from 8 to 22 carbon atoms and the lower alkyl group may have from 1 to 4 carbon atoms and alkyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride in which the alkyl radical may be iso-octyl or nonyl and in which the phenyl radical may, if desired, be substituted by a methyl radical. Various other analogs of these quaternaries may also be employed such, for example, as cetyl dimethyl ethyl ammonium bromide or oleyl dimethyl ethyl ammonium bromide.

In general, we prefer to use such quaternary ammonium compounds which have a phenol coefficient of at least 100 with respect to both *Staphylococcus aureus* and *Salmonella typhosa* at 20° C. When determined by the standard method given in the "Official Methods of Analysis of the Association of Official Agricultural Chemists," Ninth Edition (1960), page 63 et seq.

The dibasic acids used according to this invention contain predominantly thirty-six carbon atoms and are obtained commercially by the dimerization of mono-, di- and poly-unsaturated fatty acids or their esters such, for example, as the fatty acids derived from soybean oil. They are usually of highly complex structure and may be either acyclic or alicyclic in nature. These acids are known to the trade as "dimer acids" and are available, for example, from Emery Industries, Inc., under the trade name of "Empol" dimer acids. They are described in a publication of Emery Industries, Inc., entitled, "Empol Dimer Acids," dated 1963 and their chemistry is described in many scientific publications such as Bradley and Johnston, "Drying Oils and Resins," Ind. Eng. Chem. 32, 802-809 (1940) and others, some of which are summarized in Markley, "Fatty Acids," published in 1947 by Interscience Publishers, Inc., N.Y.C., pp. 328-332.

The compounds of this invention may be prepared by mixing aqueous solutions of the quaternary ammonium salts or hydroxides with an aqueous solution of the acid in question or any of its water-soluble salts.

After thorough mixing, the organic product layer is separated from the aqueous layer (as with a separatory funnel) since two distinct phases are formed. Separation may be facilitated by the addition of an organic solvent immiscible with water. The product layer may be washed

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with water to remove any residual by-product salt or unreacted materials. The solvent, if any, may be evaporated and the product air or vacuum dried to a paste, wax, oil or solid.

It is not necessary to use an aqueous medium. Any solvent or solvent mixture in which the starting materials are soluble will be satisfactory. Non-aqueous solvents facilitate the separation of by-product inorganic salt and reduce the need for vacuum drying to get an anhydrous product. When a non-aqueous medium is employed, it is usually necessary to add a small amount of water to facilitate ionic reaction.

The product may be used, if desired, without drying since any entrapped water is irrelevant to the microbiological activity of the compounds. In other applications, removal of water may be essential for reasons not related to biological activity.

An alternative method for the preparation of compounds especially applicable to the treatment of fabric, ropes, net, woven and non-woven fabric and reticulated or convoluted materials, involves a two-step process. In the first step, the material is passed through a bath containing the anionic moiety. Excess solution is removed by methods well known to those skilled in the art. The treated material is then passed through a second bath wherein the concentration of quaternary ammonium compound is such that the material pickup will result in an equivalent amount of quaternary ammonium compound reacting with the anionic moiety, depositing the product in the most intimate way on the surface and in the interstices, convolutions and reticulations of the material.

The method of adjustment of solution concentration to achieve the required pickup is well known to those skilled in the art. The order of treatment may be reversed without affecting the biological activity or durability of the product on the material. The products of this invention may be formulated as water dispersions by dissolving them in a water-miscible organic solvent such as acetone or methanol and diluting with water or by dissolving them in emulsifiable oils such as, for example, sulfonated castor oil or pine oil and diluting with water. In preparing aqueous dispersions, emulsifying agents such, for example, as ethylene oxide condensates of alkyl phenols may be used with or without organic solvents.

It is surprising that the compounds of this invention exhibit high microbiological activity despite their relative insolubility in water. Because of their unusual combination of physical and microbiological properties, they can be used to impart laundry-resistant anti-microbial characteristics to textiles. They can also be used as the active agent in antimildew finishes for textiles which are resistant to leaching with water.

Although the compounds have low water solubility, they are compatible with various organic solvents, plasticizers and high molecular weight compounds. Consequently, they may be incorporated as anti-microbial agents in synthetic resins and plastics. The compounds are compatible with natural and synthetic rubber latices. Therefore, they may be used to prepare bacteriostatic films and molded objects deposited from such latices.

The compounds can be incorporated into cutting and grinding fluids without precipitation. Also, they blend well with non-ionic and anionic surface active agents. In such compositions they retain their microbiological activity.

It will be understood that the properties of the products described herein will vary depending upon the nature of the cationic quaternary ammonium compound used in their preparation as well as the anionic compound reacted therewith.

The chemical, physical and biological properties of the products of our invention make them especially appropriate for the following applications when suitably incor-

porated in active amounts in an appropriate vehicle, binder, medium or substrate:

- (1) Mildewproofing fabric, canvas, ropes, textiles, awnings, sails tenting and other woven and non-woven reticulated materials.
- (2) Paint mildewstats.
- (3) Jet plane fuel additive to control growth of microorganisms.
- (4) Odor preservative agents for clothes and shoes.
- (5) Mildew retardant and odor suppressant for shoes and other leather products.
- (6) Topical antiseptics.
- (7) Antidandruff agents.
- (8) Disinfection agents for hair and gut of man and beast.
- (9) Bacteriostatic furniture dressing.
- (10) Surface finishes for stone, plaster, tile, cement, brick and other inorganic building materials, to retard growth of microorganisms, fungi, mold and algae.
- (11) Wool perservative.
- (12) Plant and tree spray to combat fungi.
- (13) Antimycotic agents for soap wrappers.
- (14) Self-sanitizing brushes.
- (15) Mildewproofing agent in and on plastic and film.
- (16) Mildewproofing of cellulose, cardboard, fibreboard, paper and cordage.
- (17) Contact biostat for application to film, waxes and cloth to preserve cheese, meats and vegetables and other food products.
- (18) Algal inhibition, especially on surfaces and in solution where low foaming is desirable.
- (19) Paper pulp slime control.
- (20) Sanitizing agent for rug, carpet, curtains.
- (21) Egg preservation.
- (22) Adhesive preservation.
- (23) Preservation of latex paints.
- (24) Preservation of metal-working compounds.
- (25) Additives for soap and for both anionic and non-ionic detergents in liquid, bar, powder, bead, solution and other forms to impart bacteriostatic and fungistatic properties thereto.

The microbiological activity of our compounds has been evaluated for microbiological stasis by the Standard Tube Dilution Test, the technique for which is common knowledge to those skilled in the art. A Difco Bacto CSMA Broth #0826 was used in the study. This test is used to determine the lowest concentration of microbiologically active compounds which will inhibit the growth of the organism in question. For a wide range of applications, the inhibition of growth rather than outright kill is satisfactory.

Briefly put, the Tube Dilution Test consists in placing 9 cc. of the CSMA Broth in a test tube which is then sterilized in an autoclave. One cc. solution of the microbiologically active compound at an appropriate concentration is added to the test tube which is then inoculated with 0.1 cc. of a twenty-four hours old culture of the organism under study. The test tube is then incubated at 37° C. for forty-eight hours and observed for bacterial growth.

The same procedure is followed for fungi. In such tests, however, the tubes are incubated for fourteen days at a temperature suitable for optimum fungal growth, usually 25° C.

The invention is illustrated by, but not restricted to, the following examples:

Example I

A stock solution was prepared containing 10 weight percent of the neutral sodium salt of the dimerized fatty acid supplied by Emery Industries, Inc., under the designation "Empol 1022 Dimer Acid" having an acid value of 190 and described in the aforementioned 1963 publication of the supplier.

To a vigorously agitated aliquot of this solution containing 0.23 equivalent weights of the compound was added

the chemically equivalent weight of a 10 weight percent solution of a technical grade of alkyl dimethyl ethyl benzyl ammonium chloride (Onyx Chemical Corporation's "BTC-471"; alkyl distribution: C₁₂ 50%, C₁₄ 30%, C₁₆ 17%, C₁₈ 3%).

Benzene was added to the agitated mixture and the mix then poured into a separatory funnel and allowed to separate into two phases. The organic product layer was removed and the benzene evaporated on a steam bath. The product was vacuum dried to yield a yellow paste consisting, for the most part, of the di(alkyl dimethyl ethyl benzyl ammonium) salt of the dimer acid. Approximately one-sixth of the product was the neutral salt of trimer acids present at a component of the "Empol 1022."

Biostasis was evaluated against *Staphylococcus aureus*, *Salmonella typhosa* and *Aspergillus niger* by the Standard Tube Dilution Test described above. The product showed biostasis at the dilutions shown:

20	<i>S. aureus</i> -----	1:1,000,000
	<i>S. typhosa</i> -----	1:100,000
	<i>A. niger</i> -----	1:100,000

The product of this example was found to be particularly effective in the prevention of mold growth on asphalt shingles when incorporated therein to the extent of 0.5%.

Example II

An aliquot of the stock solution of Example I containing 0.23 equivalent of the disodium salt of dimerized fatty acid was vigorously agitated while a chemically equivalent amount of a commercially available grade of alkyl dimethyl benzyl ammonium chloride (Onyx Chemical Corporation's "BTC-824"; alkyl distribution: C₁₄ 60%, C₁₆ 30%, C₁₂ 5%, C₁₈ 5%) in the form of a 10 weight percent solution was slowly added.

The agitated mixture was then poured into a separatory funnel. The mixture separated into two phases. The organic product layer was removed and vacuum dried to yield 77% of the theoretical yield of the di(alkyl dimethyl benzyl ammonium) salt of the dimer acid, containing about one-sixth of the corresponding neutral salt of trimer acids present in "Empol 1022" in the form of a yellow paste.

Biostasis was evaluated against *Staphylococcus aureus*, *Salmonella typhosa* and *Aspergillus niger* by the Standard Tube Dilution Test described above. The product showed biostasis at the dilutions shown:

50	<i>S. aureus</i> -----	1:10,000,000
	<i>S. typhosa</i> -----	1:10,000
	<i>A. niger</i> -----	1:10,000

Example III

An aliquot of the stock solution of Example I containing 0.23 equivalent of the disodium salt of dimerized fatty acids, "Empol 1022," was vigorously agitated while a chemically equivalent amount of lauryl isoquinolinium bromide (Onyx Chemical Corporation's "Isothan Q-75") was slowly added in the form of a 10% weight solution.

The agitated mixture was then poured into a separatory funnel, allowed to separate and the organic layer removed and vacuum dried. A dark brown paste consisting largely of the di(lauryl isoquinolinium) salt of dimer acids, together with lesser amounts of the tri(lauryl isoquinolinium) salt of trimer acids was obtained in a 70.6% theoretical yield.

Biostasis was evaluated against *Staphylococcus aureus*, *Salmonella typhosa* and *Aspergillus niger* by the Standard Tube Dilution Test described above. The product showed biostasis at the dilutions shown:

70	<i>S. aureus</i> -----	1:100,000
	<i>S. typhosa</i> -----	1:10,000
75	<i>A. niger</i> -----	1:10,000

We claim:

1. The reaction product of a water soluble alkyl quaternary ammonium compound having a phenol coefficient of at least 100 with respect to both *Staphylococcus aureus* and *Salmonella typhosa* at 20° C. and a water soluble commercial dimerized fatty acid having an acid value of 190 and having predominantly 36 carbon atoms obtained by dimerization of an alphatic compound selected from the group consisting of mono-, di- and poly-unsaturated fatty acids and esters thereof.

2. The di(alkyl dimethyl ethyl-benzyl ammonium) salt of a dimerized fatty acid having an acid value of 190 wherein the alkyl group has 50% C₁₂, 30% C₁₄, 17% C₁₆ and 3% C₁₈ carbon atoms.

3. The alkyl dimethyl benzyl ammonium salt of a dimerized fatty acid having an acid value of 190 wherein the alkyl group has 60% C₁₄, 30% C₁₆, 5% C₁₂ and 5% C₁₈ carbon atoms.

4. The lauryl isoquinolinium salt of dimerized fatty acids having an acid value of 190.

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