

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, for example, as 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 microbiocidal 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 anti-mildew 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.

The compounds of this invention also possess effective antistatic properties and may be incorporated in or used as a coating upon any product that is subject to static electricity. For example, they may be used to coat or impregnate wood, paper, ceramics, natural or synthetic polymers, etc. They may be coated upon the surface of such products or intermixed with the components of a molded, cast or extruded product.

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 incorporated 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 preservative.
- (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.
- (26) Antistatic coatings and impregnants.

The microbiocidal 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 hour 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 10% aqueous solution of the sodium salt of nitro-cyclohexane, which may be made by reacting cyclohexane with dilute nitric acid and which is also available commercially from the Aldrich Chemical Co., Inc. Milwaukee, Wis., was prepared, and 130 grams of this solution was placed in a separatory funnel. To this solution was added 350 grams of a 10% solution of lauryl isoquinolinium bromide (Onyx Chemical Corporation's "Isothan Q-75") and 100 ml. of benzene. The funnel was shaken and then layer separation allowed to occur. The benzene layer was separated and dried first on a steam bath and then in a vacuum oven to give 38 grams (99% yield) of a dark red syrup of lauryl isoquinolinium nitro-cyclohexane enolate.

EXAMPLE II

An additional 130 grams of the nitrocyclohexane solution described in Example I was placed in a separatory funnel and 320 grams of a 10% solution of alkyl dimethyl ethylbenzyl ammonium chloride (Onyx Chemical Corporation's "BTC-471"; alkyl distribution: C₁₂, 50%;

C₁₄, 30%; C₁₆, 17%; C₁₈, 3%) was added along with 100 ml. of benzene. The funnel was shaken and the benzene layer separated and dried to give 37 grams (89% yield) of a yellow paste of alkyl dimethyl ethylbenzyl ammonium nitrocyclohexane enolate.

EXAMPLE III

160 grams of a 10% solution of the potassium salt of 1-nitrododecane, which may be prepared similarly to the nitrocyclohexane of Example I, was placed in a 1 liter separatory funnel together with 260 grams of a 10% solution of the quaternary ammonium compound shown in Example II. After 100 ml. of benzene was added, the funnel was well shaken. Layer separation was allowed to occur and the benzene layer separated and dried to give 35 grams (97% yield) of an orange paste of alkyl dimethyl ethylbenzyl ammonium nitrododecane enolate.

To an additional 100 grams of the nitrododecane solution was added a chemically equivalent amount of alkyl dimethyl benzyl ammonium chloride (Onyx Chemical Corporation's "BTC-824"; alkyl distribution: C₁₄, 60%; C₁₆, 30%; C₁₂, 5%; C₁₈, 5%). Benzene was added and the solutions mixed. The product was worked up as above to give 149 grams (100% yield) of a yellow paste of alkyl dimethyl benzyl ammonium nitrododecane enolate.

Using the quaternary ammonium compound of Example I, a dark red viscous liquid of lauryl isoquinolinium nitrododecane enolate, in 98% yield, was obtained from 1-nitrododecane.

EXAMPLE IV

To 1 mol of undecenyl alcohol containing 0.5 cc. of pyridine and kept in an ice-salt mixture, there was added slowly, with stirring, 2 mols of thionyl chloride. The mixture was heated at 130°-140° C. until evolution of sulfur dioxide ceased. The excess of thionyl chloride was distilled off under diminished pressure and the residue was washed first with saturated aqueous sodium chloride solution, then with 10% aqueous sodium carbonate solution, and, finally, again with the sodium chloride solution. The oil was taken up in ether, the solution was dried and distilled under reduced pressure to yield 83% of 10-undecene 1-chloride. This product was reacted with silver nitrite in the manner described in "The Journal of the American Chemical Society," vol. 51, page 279 (1929), to obtain 1-nitro-10-undecene. This product was then brominated in the standard manner to obtain 1-nitro-10,11-dibromoundecane, which was then dehydrobrominated by the action of caustic potash to potassium salt of 1-nitro-10,11-undecyne.

Stoichiometric amounts of the 1-nitro-10,11-undecyne and "BTC-471 (disclosed in Example II) were reacted in the same manner, and using the same procedures as in Example II, to yield a dark, viscous product identified as alkyl dimethyl ethyl-benzyl ammonium 1-acinitroundecyne.

EXAMPLE V

A 10% solution of the sodium salt of 2-nitro-1-butanol was prepared and reacted with a chemically equivalent amount of a 10% solution of lauryl isoquinolinium bromide. Extraction with benzene and drying yield a 100% yield of a red-brown paste of lauryl isoquinolinium 2-nitro-1-butanol enolate.

EXAMPLE VI

Using the general procedure and the quaternary ammonium compounds of Examples I-V, the potassium salt of beta nitrostyrene was reacted with lauryl isoquinolinium bromide (red paste—98% yield), alkyl dimethyl benzyl ammonium chloride (orange paste—61% yield) and alkyl dimethyl ethylbenzyl ammonium chloride (orange solid—98% yield).

The latter two derivatives were subjected to the Agar Plate Test to determine zones of inhibition of growth against *Staphylococcus aureus* (S.a.), *Salmonella typhosa*

(S.t.) and *Aspergillus niger* (A.n.). Zones were obtained as shown in Table I.

TABLE I

Beta nitrostyrene reaction—product with—	Zones of inhibition, mm.		
	S.a.	S.t.	A.n.
Alkyl dimethyl ethylbenzyl ammonium chloride.....	10.8	4.2	15.8
Alkyl dimethyl benzyl ammonium chloride.....	28.26	7.0	26.24

EXAMPLE VII

Two of the quaternary-nitro aliphatic reaction products were run against *Desulfovibrio desulfuricans* according to the procedure outlined in the report of the American Petroleum Institute Subcommittee on Biological Analysis of Injection Waters To Be Used for Water Flood Purposes (March 17, 1958).

Reaction product of lauryl ethylbenzyl dimethyl ammonium chloride with—	Bacteriostatic level vs. <i>Desulfovibrio desulfuricans</i> (p.p.m.) at—
Sodium nitrocyclohexane.....	5.0
Potassium 1-nitrododecane.....	7.5

EXAMPLE VIII

Using the Standard Tube Dilution Test described above, the following bacteriostatic levels were determined (S.a.=*Staphylococcus aureus*; S.t.=*Salmonella typhosa*; A.n.=*Aspergillus niger*):

Product form—	Bacteriostatic dilution level vs.		
	S.a.	S.t.	A.n.
Example I.....	10 ⁵	10 ⁴	10 ³
Example II.....	10 ⁶	10 ⁵	10 ⁴
Example IV.....	10 ⁷	10 ⁶	10 ⁴

Obviously, many modifications and variations of the present invention are possible in the light of the above teachings. It is, therefore, to be understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

The invention claimed is:

1. A quaternary ammonium compound having a quaternary cation selected from the group consisting of alkyl dimethyl benzyl ammonium, alkyl dimethyl ethylbenzyl ammonium and alkyl isoquinolinium, wherein the alkyl, in each instance, has 12 to 18 carbon atoms, and having an anion selected from the group consisting of mono-acinitrocyclohexane, 1-acinitrododecane, 2-acinitro-1-butanol, beta-acinitrostyrene and 1-nitro-10,11-undecyne.

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