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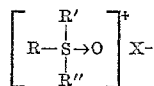
3,196,184

SULFOXONIUM COMPOUNDS

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This invention relates to a new class of sulfur-containing cationic antibacterial surfactant compounds. More particularly, this invention relates to sulfoxonium compounds corresponding to the following structural formula:



wherein

R is an aliphatic radical containing from about 10 to about 20 carbon atoms which can be saturated or unsaturated, branched or straight chain.

R' and R'' are each selected from the group consisting of lower alkyl, benzyl, halogenated benzyl and alkylbenzyl, wherein the alkyl substituent contains from 1 to about 4 carbon atoms, and wherein

X is an anion which permits adequate solubility of the sulfoxonium salt. Suitable examples of such anions are halide, sulfate, methosulfate, p-toluene sulfonate, and nitrate radicals.

A vast variety of chemical compounds has been studied from the standpoint of surface activity (note for example, A. M. Schwartz, J. W. Perry and Julian Birch, "Surface Active Agents and Detergents," published by Interscience Publishers, Inc., New York, 1958). There appears, however, to have been no recognition before this invention of the sulfur-containing surface-active compounds corresponding to the above described structural formula; nor have the detergency properties of these compounds been known. Moreover, it was quite unexpected to discover that this class of cationic surfactants would combine the features of efficiency in bacteriostasis with excellent mildness on the skin and compatibility with other types of surfactant detergents.

Thus, the compounds of the present invention are characterized by a unique combination of properties including adequate solubility in water, high bacteriostatic effectiveness, substantially odorless, having low volatility, high stability, and as mentioned, exceptional mildness. Most prior art compounds which are structurally related to the sulfoxonium compounds of this invention do not present these combined properties. For instance, reference may be made to sulfonium salts which are prepared by the alkylation of dialkyl thioethers. The crude sulfonium salts often contain small amounts of odorous thioethers which are objectionable. The sulfoxonium salts described herein which are prepared by alkylation of odorless sulfoxides do not present such problems. Of especial significance is the discovery that the novel cationic compounds described herein are compatible with other detergent surfactant compounds such as anionic, cationic and nonionic surfactant compounds. This is contrary to numerous references in the prior art which uniformly warn against mixing anionics with cationics.

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Representative of such references is a discussion contained in Kirk and Othmer, Encyclopedia of Chemical Technology, volume 13, p. 528, which notes that "one disadvantage of cationic surface-active agents, either when used as such or as bactericides, is that they are incompatible with soaps or other anionic surface-active compounds." In contrast to this widely held statement, it has been found that the sulfoxonium salts of this invention do not lose their bacteriostatic activity with anionic surfactants.

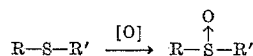
An object, therefore, of this invention is to provide a new and useful class of cationic surfactant compounds. A further object is to provide a new class of sulfur containing cationic surfactants whose members characteristically combine high bacteriostatic effectiveness and exceptional mildness on the skin and which are also compatible with other types of surfactants. An additional object is to provide a new class of high molecular weight sulfoxonium antibacterial surfactants which are produced as the S-alkylation products of dialkyl sulfoxides. Yet a further object is to produce a new and improved bacteriostatic composition comprising an organic water soluble detergent surfactant and a cationic sulfoxonium compound produced according to this invention. Another object is to provide detergent compositions containing sulfoxonium compounds of the present invention. Other objects will become apparent as the invention is hereinafter described in detail.

The compounds of this invention have the following general formula: $[RR'R''S(O)]^+X^-$ where R is a high molecular weight, saturated or unsaturated, branched or straight chain aliphatic radical having from about 10 to about 20 carbon atoms. As suitable long chain saturated alkyl radicals used alone or in admixture there can be mentioned, as examples, decyl, dodecyl, tetradecyl, hexadecyl, and eicosenyl. Examples of alkenyl radicals also used alone or in admixture are decenyl, dodecenyl, tetradecenyl, hexadecenyl, octadecenyl and eicosenyl.

R' and R'' can each be lower alkyl such as, for example, methyl, ethyl, propyl, butyl, amyl, and hexyl benzyl, halogenated benzyl, and alkylbenzyl in which the alkyl substituent contains from 1 to about 4 carbon atoms. The nature of the anionic substituent, X, is discussed later on in this specification.

The novel compounds described herein are prepared, for example, by condensing an R,R' dialkyl sulfoxide, with a suitably active R''X alkylating agent. The end result of the reaction is that the alkyl radical of the alkylating agent attaches to the sulfur atom of the sulfoxide and the anionic group X of the alkylating agent becomes the anionic constituent in the sulfoxonium product. These new sulfoxonium compounds bear a general similarity to quaternary ammonium compounds. As will be pointed out, however, the properties of the quaternary ammonium compounds differ materially from the compounds of this invention.

The sulfoxide starting material can be obtained by oxidizing a dialkyl sulfide or thioether according to the following equation:



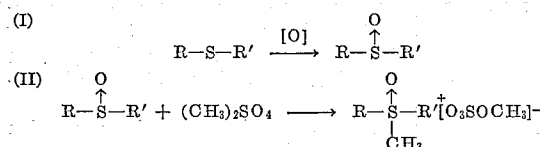
This is a relatively well known oxidizing process requiring generally mild reaction conditions. As the oxidiz-

ing agent, various agents can be employed such as hydrogen peroxide, nitric acid and nitrogen oxides such as nitrogen tetroxide.

On oxidation, one oxygen equivalent of reagent converts a starting dialkyl sulfide into the corresponding dialkyl sulfoxide. Care must be taken to prevent the formation of sulfones in this preparation as a second equivalent of an oxidizing reagent produces the sulfones. The use of nitric acid permits quite selective oxidation to the sulfoxide.

In the resulting dialkyl sulfoxide structure, the coordinate link between the sulfur and the oxygen is a semi-polar double bond, unlike that of carbonyl, $C=O$, grouping. Accordingly, an arrow is used to identify this feature in place of a double bond.

The preparation of the new compounds of this invention is illustrated by the following reaction equations.



wherein the R and R' are each as described earlier in this specification. The foregoing is not intended as a limitation imposed upon the method of preparing the new sulfoxonium compounds. For instance, in a contemplated variation a sulfoxide such as $R'R''S(O)$ is alkylated by RX, with R being a long chain saturated or unsaturated straight or branched chain aliphatic radical containing from about 10 to 20 carbon atoms, provided, of course, that RX possesses sufficient activity as an alkylating agent.

The preferred embodiments of the present invention include compounds of the foregoing general formula in which R is a high molecular weight, long chain aliphatic radical, saturated or unsaturated, branched or straight chain containing from 10 to 20 carbon atoms. The more especially preferred compounds are obtained when R contains from 12 to 18 carbon atoms in the alkyl chain corresponding to chain length occurring, for example, in natural fatty materials. When chain lengths containing below 10 carbon atoms are obtained, it has been discovered that the surface active properties of the compound tend to diminish, and when the chain length exceeds about 20 carbon atoms, a solubility problem is presented due to the increasing insolubility of the compounds.

R' and R'' can be either lower alkyl radicals, e.g. those containing from 1 to 6 carbon atoms, benzyl, halogenated benzyl and alkyl benzyl radicals containing from 1 to about 4 carbon atoms in the alkyl substituent. Preferred compounds are obtained when R' and R'' are each selected from methyl, ethyl, propyl, butyl, benzyl, chlorinated benzyl and methylbenzyl radicals.

The exact nature of the anionic portion is thought to be immaterial so far as the bacteriostatic properties of the new compounds are concerned. Accordingly, virtually any organic or inorganic anion which permits adequate solubility of the sulfoxonium salt may be found suitable, determined fairly well by availability and cost factors. Interconversion of one anion for another by well-known methods may be advantageous and is permissible. Examples of anionic groupings which have shown value in the new compounds are halides (e.g. chloride, bromide, iodide, fluoride), sulfates, methosulfate, p-toluene sulfonates and nitrates.

Brief reference has been made to the requisite reactivity of the alkylating agent. The reason for this may be apparent, but for purposes of complete understanding it should be understood that dialkyl sulfoxides are relatively difficult to alkylate. Accordingly, use of a reactive alkylating agent exemplified by dimethyl sulfate is preferred. Less reactive alkylating agents such as alkyl halides, and particularly chlorides and bromides, frequently give poorer results. Furthermore, with some alkylating agents forma-

tion of the kinetically favored but less stable O-alkyl adduct occurs and long equilibration to convert these to the S-alkyl compound is required. (See S. G. Smith and S. Winstein, *Tetrahedron*, 3, 319 (1958).) For this reason, reagents such as alkyl nitrates and p-toluene sulfonates, while operative, are less generally useful than reagents such as dimethyl sulfate.

The following sulfoxonium compounds, none of which are known to be described in the prior art are exemplary of those which can be prepared substantially as described herein:

Decyl dimethyl sulfoxonium iodide
Dodecyl dimethyl sulfoxonium iodide
Tetradecyl dimethyl sulfoxonium iodide
Hexadecyl dimethyl sulfoxonium iodide
Octadecyl dimethyl sulfoxonium iodide
Dodecenyl dimethyl sulfoxonium iodide
Decyl methyl benzyl sulfoxonium chloride
Dodecyl methyl benzyl sulfoxonium bromide
Dodecyl methyl benzyl sulfoxonium methosulfate
Dodecyl methyl o-chlorobenzyl sulfoxonium methosulfate
Dodecyl methyl p-methylbenzyl sulfoxonium methosulfate
Dodecyl methyl p-butyl benzyl sulfoxonium methosulfate
Tetradecyl dimethyl sulfoxonium methosulfate
Tetradecyl methyl benzyl sulfoxonium p-toluene sulfonate
Tetradecyl methyl benzyl sulfoxonium nitrate
Tetradecyl methyl benzyl sulfoxonium sulfate
Tetradecenyl dimethyl sulfoxonium chloride
Dodecyl butyl benzyl sulfoxonium methosulfate
Hexadecyl dimethyl sulfoxonium methosulfate
Hexadecyl methyl benzyl sulfoxonium methosulfate
Hexadecyl butyl o-chlorobenzyl sulfoxonium methosulfate
Hexadecyl methyl p-methyl benzyl sulfoxonium iodide
Hexadecyl methyl p-ethyl benzyl sulfoxonium nitrate
Hexadecenyl methyl p-methyl benzyl sulfoxonium methosulfate
Octadecyl dimethyl sulfoxonium iodide
Octadecyl dimethyl sulfoxonium methosulfate
Octadecyl methyl benzyl sulfoxonium p-toluene sulfonate
Octadecyl methyl o-chlorobenzyl sulfoxonium chloride
Octadecyl butyl p-methylbenzyl sulfoxonium sulfate
Octadecenyl dimethyl sulfoxonium iodide
Octadecyl propyl benzyl sulfoxonium nitrate
Dodecyl dimethyl sulfoxonium methosulfate
Eicosyl dimethyl sulfoxonium methosulfate

The foregoing list is not intended to be exclusive and is only exemplary of the broad scope of the invention. Accordingly, it is intended that the full breadth of this invention encompasses all compounds which can be synthesized in conformity with the above described general formula.

The following specific examples are also merely illustrative and are not to be construed in any way as limiting the scope of the invention.

EXAMPLE I

Dodecyl dimethyl sulfoxonium methosulfate

11.2 grams of dodecyl methyl sulfoxide (0.031 mole) and 4.3 grams of dimethyl sulfate (0.034 mole) were combined and heated to 95° C. on a steam bath for 18 hours. The flask was swept with nitrogen gas during the initial heating and then protected with a calcium chloride filled drying tube. About 50 ml. acetone was added to the cooled reaction mixture, and resulting dark colored solution chilled in a Dry Ice-acetone bath, and the product harvested by filtration. The product was redissolved in 50 ml. acetone containing a few milliliters of methanol to enhance solubility, and decolorized by refluxing with Nuchar charcoal. Following filtration, the filtrate was chilled in a Dry Ice-acetone bath and the resulting white crystals of dodecyl dimethyl sulfoxonium methosulfate harvested by filtration. The product melted at 117-120° C., and analysis by titration with standard alkylbenzene sulfonate solution established its purity at

95.3%. The products had surface active properties and bacteriostatic activity coupled with mildness to the skin as determined by tests described in the discussion following the examples.

The corresponding octadecyl compound can be prepared in essentially the same manner using equivalent quantities of reactants and the resulting octadecyl dimethyl sulfoxonium methosulfate possesses surface activity and bacteriostatic properties. Related compounds having similar properties and containing ten carbon atoms or a carbon chain length intermediate the C₁₂-C₁₈ range can also be prepared by following this example.

EXAMPLE II

Hexadecyl dimethyl sulfoxonium methosulfate

10 grams (0.034 mole) of hexadecyl methyl sulfoxide was added to 4.67 grams (0.037 mole) of dimethyl sulfate. The mixture was heated to 90° C. in a steam bath for about 48 hours. The product was dissolved in 75 ml. acetone containing a few milliliters of methanol to form a solution which was cooled in an ice bath. A crystalline product so obtained was redissolved in a methanol-acetone mixture. Nuchar treated to remove coloring, and recrystallized. The product, recovered as hexadecyl dimethyl sulfoxonium methosulfate, M.P. 125° C. and 98% pure by titration, was surface active and had bacteriostatic activity.

EXAMPLE III

Dodecyl methyl o-chlorobenzyl sulfoxonium methosulfate

Dodecyl methyl o-chlorobenzyl sulfoxonium methosulfate was obtained by allowing 20 grams (0.058 mole) of dodecyl o-chlorobenzyl sulfoxide of M.P. 44-46.5° C. to react with 14.7 grams (0.117 mole) of dimethyl sulfate at a temperature of 99° C. The same pattern of the previous examples was followed. This product, in common with some other benzyl substituted sulfoxonium salts, was poorly crystalline. Instead of isolation in crystalline form, this material was used in the form of an aqueous suspension which could be assayed by direct titration with standard alkylbenzene sulfonate solution. A dry sample of the product indicated 94% purity on titration, and has surface active and bacteriostatic properties.

EXAMPLE IV

Dodecyl methyl benzyl sulfoxonium methosulfate

Dodecyl methyl benzyl sulfoxonium methosulfate was prepared by bringing together 17.9 grams (0.058 mole) of dodecyl benzyl sulfoxide (M.P. 79-81° C.) and 14.6 grams (0.116 mole) of dimethyl sulfate and following the procedure outlined previously in Example I. Isolation of the dodecyl methyl benzyl sulfoxonium methosulfate yielded a product assaying 100% pure by titration. The product had surface active and bacteriostatic properties.

EXAMPLE V

Dodecyl methyl p-methyl benzyl sulfoxonium methosulfate

Methylation of dodecyl p-methylbenzyl sulfoxide (M.P. 74-77° C.) with dimethyl sulfate using a method analogous to that of Example I, resulted in the formation of dodecyl methyl p-methylbenzyl sulfoxonium methosulfate. Purity established by titration was 91.7%. The compound exhibited surface active and antimicrobial effectiveness.

EXAMPLE VI

Hexadecyl methyl benzyl sulfoxonium methosulfate

Reaction of 20 grams (0.055 mole) of hexadecyl benzyl sulfoxide of M.P. 90-91° C. with 13.9 grams (0.11 mole) of dimethyl sulfate in a manner analogous to that of Example I resulted in hexadecyl methyl benzyl sulfoxonium

methosulfate. Purity by titration was 99.5%. The compound when tested presents surface activity and bacteriostatic value.

EXAMPLE VII

Tetradecyl dimethyl sulfoxonium methosulfate

Reaction of 10 grams (0.038 mole) of tetradecyl methyl sulfoxide and 5.3 grams (0.042 mole) of dimethyl sulfate, provided, in a manner analogous to that of Example I, tetradecyl dimethyl sulfoxonium methosulfate, of M.P. 124° C. and 95.4% purity.

The alkylation reaction generally is conducted on an equimolar basis. To insure completion, an excess of the alkylating agent can be used, especially if it is one of relatively lower reactivity. The temperature during the alkylation usually is between 80 and 120° C. and at atmospheric pressure. With the less reactive alkyl halides use of pressure vessels and of temperatures between 100-150° are preferred.

As indicated previously, the sulfoxonium compounds described herein have been discovered to be valuable bacteriostatic agents. The antibacterial activity of these compounds was determined by conducting "Standard Tube Dilution Tests." Such tests are conducted in vitro and consist essentially of preparing test tubes of a standardized broth medium containing serial dilutions (diminishing concentrations) of a compound being tested, inoculating each tube with a preselected microorganism and after an incubation period, determining the growth of bacteria in each tube.

The broth medium employed in these assay tests was an FDA phenol coefficient test nutrient broth. Stock solutions of the test product were then prepared in sterile distilled water. Serial dilutions were prepared of the test stock solution and then placed into the contact tubes containing the nutrient broth.

The contact tubes were then inoculated with bacterial organisms prepared in the following manner. A washed 24 hour broth culture of gram-positive *Staphylococcus aureus* ATCC 6538 was standardized to a predetermined optical density, by dilution with sterile FDA nutrient broth, to contain about 500,000,000 organisms per milliliter. One-tenth milliliter quantities of the standardized inoculum were added per each previously prepared contact tube. Gram-negative *Escherichia coli* ATCC 26 cultures were prepared as inoculum in a similar manner.

Of the four contact tubes thus prepared at each serial dilution tested, three were inoculated and one was retained as an uninoculated control.

The inoculated tubes were shaken thoroughly, allowed to stand 10 minutes for air bubbles to disperse, then read for a zero-hour turbidity value using a Coleman Junior Model 6A spectrophotometer set at a wave length of 610 millimicrons.

After 24 hours of incubation at 37° C. the tubes were again shaken, allowed to stand for ten minutes, and then read to obtain 24 hour turbidity values. Differences in turbidity values are used as a measure of growth of the bacteria in the contact tubes. In this manner, there was determined the minimum effective concentration of the antibacterial which prevented growth of the organism during incubation. This concentration (parts per million of bacteriostatic agent) is called the bacteriostatic breakpoint.

In order to allow for a comparison of the relative bacteriostatic effectiveness of the novel sulfoxonium compounds, similar in vitro tests were run with a well known and widely used organic anionic surfactant compound, sodium dodecylbenzene sulfonate, commonly referred to as alkyl benzene sulfonate or ABS. The alkyl benzene sulfonate employed was the sodium salt of the sulfonic acid derived from the condensation product of benzene and propylenes having from 9 to about 15 carbon atoms and averaging 12 carbon atoms. Alkyl benzene sulfonate is probably one of the most widely used synthetic deter-

gent surfactants and one which is regarded as having relatively good bacteriostatic effectiveness. Compounds which evidence substantially greater antibacterial effectiveness than alkyl benzene sulfonate are considered in the art to be good bacteriostats and as such are always in great demand for manifold useful purposes.

The results of the in vitro tests described above are tabulated in Table I.

TABLE I

Test Material	Breakpoints ¹ (at p.p.m. for control)	
	<i>Staphylococcus aureus</i> ATCC 6538	<i>Escherichia coli</i> ATCC 26
Dodecyl dimethyl sulfoxonium methosulfate	9.4	50.0
Tetradecyl dimethyl sulfoxonium methosulfate	1.86	28.1
Hexadecyl dimethyl sulfoxonium methosulfate	2.89	25.0
Dodecyl methyl benzyl sulfoxonium methosulfate	2.4	19.0
Dodecyl methyl o-chlorobenzyl sulfoxonium methosulfate	9.0	37.5
Dodecyl methyl p-methylbenzyl sulfoxonium methosulfate	2.4	19.0
Hexadecyl methyl benzyl sulfoxonium methosulfate	1.6	25.0
Dodecyl benzene sodium sulfonate	37.5	100.0

¹ The breakpoint values are averages of the three contact tubes prepared at each serial dilution.

As evidenced by the data in Table I, the members of the new class of compounds possess marked bacteriostatic effectiveness as each was found to be superior to alkyl benzene sulfonate. As the findings indicate, the compounds of this invention are especially potent against gram-positive type of organisms such as *Staphylococcus aureus* ATCC 6538. This bacteria is one most commonly found on human skin and, in the art, it is regarded as being representative of the entire field of gram-positive types of microorganisms.

Against a selected representative of the gram-negative class of microorganisms, the new compounds described herein are seen to be less effective than against the gram-positive microorganism, but in any event, they are substantially superior to alkyl benzene sulfonate.

In view of the general structural similarity between the compounds of this invention and quaternary ammonium cationic surfactants, they might be expected to share common physical properties. Therefore, since the quaternary ammonium cationics have a rather harsh and irritating effect upon human skin, it should be anticipated that the instant sulfoxonium compounds would behave similarly. Unexpectedly, however, the compounds prepared according to this invention have been discovered to be extremely mild on human skin. This exceptional behavior is an extremely desirable and useful property since it affords compounds offering a unique blend of properties, i.e. bacteriostatic effectiveness and excellent mildness characteristics.

The effect which these new compounds have upon human skin was determined by conducting a fairly standardized guinea pig immersion test. In these tests, groups of three guinea pigs which had their abdomens shaved were immersed up to the thorax in a .2% aqueous solution of the test material. The bath was maintained at a constant temperature of about 37° C., and the immersion periods were for 4½ hours at the same period of time on each of three consecutive days. The readings were made about 72 hours after the conclusion of the third exposure.

Each pig after exposure to the bath is assigned a relative skin grade value based on a range of 1 to 10. Within this range increasing mildness is represented by higher numerical values. Accordingly, a value of 1 indicates bleeding and skin fissures while a value of 10 represents the ultimate in mildness.

Intermediate values, for example, going from 2 to 9 represent increasing mildness. In exaggerated tests where human subjects are employed, a value of 1 indicates rather severe redness and dryness of the skin. Thus, the exaggerated exposure tests on animals are much more extreme than comparable tests on human subjects.

TABLE II
[Mildness tests]

Test Material	Skin Grades		
	Guinea Pig No. 1	Guinea Pig No. 2	Guinea Pig No. 3
Dodecyl dimethyl sulfoxonium methosulfate	9	9	9
Hexadecyl dimethyl sulfoxonium methosulfate	10	10	10

Guinea pigs immersed in aqueous solutions of equal concentration of quaternary ammonium cationics usually receive grade values in the range of 4 to 6 which indicates that substantial scaling and redness has resulted.

The new sulfoxonium compounds, in addition to having the unique combination of properties discussed above, offer a still further unexpected property; namely, that the members of this new series of sulfoxonium compounds that retain their antibacterial properties when combined with cleaning compositions such as fatty acid soaps and organic synthetic surfactant detergent formulations. Very frequently antibacterials lose their effectiveness in the presence of such materials with which they are combined.

Several experiments were conducted to illustrate the compatibility that exists between the new compounds described herein and representative soaps and organic detergent surfactant compounds. While illustrating the compatibility feature, the experimental data presented below in a series of examples also exemplifies the usefulness of the new compounds.

The experiments which were conducted to discover the compatibility of the sulfoxonium compounds with various classes of surfactants followed a procedure only relatively recently developed. It has been fully presented in an article published in Applied Microbiology, volume 10, No. 1, January 1962, entitled "A Method for the Determination of the Antimicrobial Properties of Treated Fabrics," by Herbert Quinn, and is referred to hereinafter as the Quinn process.

This procedure was actually designed for evaluating the effectiveness of bacteriostatic agents in retarding growth of contaminating organisms on fabrics. The method consists of direct inoculation of the treated fabric with suitable test organisms and the subsequent enumeration of growing colonies which develop when the fabric is implanted and incubated in a nutrient medium.

While the aforementioned article should be consulted for complete details of the prescribed procedure, a rather thorough description at this point will be helpful. One-square-inch fabric swatches are treated with a bacteriostatic compound in any desired manner. For instance, the fabrics may be treated by a conventional textile finishing "padding" process. For purposes of this invention, however, the fabric was treated with the antimicrobial agent via a laundering cycle using a detergent formulation containing the bacteriostatic compound being tested.

Care is taken within practical limits to insure that the fabric swatches remain in a sterile condition after treatment with the antimicrobial agent until the moment of inoculation with the test microorganism. After being laundered, the treated swatches are placed into a drying chamber where they are impregnated with 0.1 ml. of a previously prepared diluted inoculum by means of a pipette. The quantity of inoculum is regarded as being fairly critical, the idea being that the swatches should be

thoroughly saturated and yet not be dripping wet. The drying chamber is then immediately closed and the fabrics are dried in sterile warm flowing air. The dried swatches are next planted with the inoculated surface up onto a solidified sterile agar medium in previously prepared Petri dishes. An overlay of nutrient is then made by pouring 0.2 ml. to 0.3 ml. of cooled (42–45° C.) molten agar medium over the fabric. This embeds the cloth under a thin film of agar nutrient. It is of paramount importance that a thin film be used and that it be applied very carefully to avoid flushing off those organisms loosely fixed to the fabric.

When the overlay has solidified, the plates are incubated at 37° C. for about 48 hours. Colony counts are then made by means of a low-power (23×) dissecting microscope, using a wire grid with spacings of 3 mm. to facilitate counting of the colonies. The entire cloth swatch is counted when less than several hundred colonies develop. However, when the colony density is heavy, five 9-mm.² areas are counted, a factor of 71 is applied to the average value to obtain the colony count per square inch of cloth. In most experiments, six replicate swatches are inoculated with each organism.

A wide variety of inoculating organisms can be employed in the test but for the purposes of this invention, *Staphylococcus aureus* ATCC 6538, was used as a representative of the gram-positive class of organisms and *Escherichia coli* ATCC 26 was used as a representative of the class of gram-negative organisms. Both of these are commonly found among the microorganisms on human skin.

EXAMPLE 8

The foregoing procedure was followed in which the detergent composition used during the laundering cycle of the fabric swatches was a standardized detergent washing formulation in which the active organic anionic detergent surfactant compound was sodium tallow alkyl glyceryl ether sulfonate. The tallow alkyl glyceryl ether sulfonate was prepared according to the method described in Whyte Patent 2,989,547, issued June 20, 1961. The composition of the detergent composition was about 17.5% tallow alkyl glyceryl ether sulfonate, 50.0% sodium tripolyphosphate, 6% sodium silicate 14.2% sodium sulfate, the balance being water. All percentages are by weight.

Fabric swatches were first washed in 20 milliliters of a .25% washing solution of the above composition. They were then dried, placed into the prescribed drying chamber, and inoculated with 0.1 ml. solution of a diluted *Staphylococcus aureus* ATCC 6538. After drying, the swatches were implanted on a solidified sterile agar medium in a previously prepared Petri plate in the following manner. The dried swatches were placed on the solid agar medium and an overlay of nutrient having a thickness of approximately 0.1 mm. was made by pouring 0.2 to 0.3 ml. of cooled (42–45° C.) molten sterile agar medium over the fabric. As the overlay solidified the cloth thus became embedded between a thin film of nutrient base agar and the solidified sterile agar medium in the Petri plate. Next the plates were incubated at 37° C. for 48 hours after which the colony counts were made by means of a low (23×) dissecting microscope, using a wire grid with spacings of 3 mm. (stainless steel wire 0.008 in. in diameter) to facilitate counting the colonies. Six replicate swatches were inoculated with each organism and an average colony growth determined. To obtain a control figure in the present test, the above described standardized washing preparation was used, and a colony count of 3500 was obtained.

The same procedure was repeated but this time a bacteriostatic compound of this invention was employed in conjunction with the detergent preparation. In this run, 1 milligram of dodecyl methyl benzyl sulfoxonium methosulfate was used as the bacteriostatic compound to be tested. This amounted to 2% by weight of the detergent composition. After inoculation and incubation, a colony

count of about 1300 was determined, down from about the 3500 figure obtained when no bacteriostatic agent was employed. This represents an improved control of bacterial growth of almost 63%, evidencing a marked degree of compatibility between the organic anionic detergent surfactant in the detergent composition; i.e., sodium tallow alkyl glyceryl ether sulfonate and the novel cationic surfactant, dodecyl benzyl methyl sulfoxonium methosulfate. Moreover, the superior washing performance of the standardized detergent formulation was not adversely affected by the addition of the bacteriostatic compound. Thus, a superior washing product is obtained.

The experiment was repeated a third time with a lesser concentration of the sulfoxonium compound than occurred in the previous test run. In this test only 1% of the sulfoxonium compound was added based on the weight of the detergent composition employed.

In this third run a colony count of about 1800 was obtained. This represents a colony count of only 50% of that obtained without any of the novel sulfoxonium bacteriostatic compound being present. Again the washing levels of the standardized detergent composition remained excellent.

Three calculations were similarly obtained against a gram-negative organism, *Escherichia coli* ATCC 26. In an initial run, a colony count was obtained using just the detergent formulation without a sulfoxonium antimicrobial compound of this invention being present. A second test run was performed in the presence of 2% concentration by weight of a sulfoxonium compound of this invention, i.e., dodecyl methyl benzyl sulfoxonium methosulfate.

The colony count for the detergent preparation alone was about 3800. At 2% concentration of the sulfoxonium compound the count factor dropped to about 1900, an improvement in growth control of the gram-negative organism of about 50%. At 1% concentration, comparable results were obtained. It is generally agreed in the art that the gram-negative bacteria are more difficult to control than the gram-positive organisms. Thus, as shown in this example, the gram-negative organisms were indeed more resistant than the gram-positive, yet compatibility is still present between the anionic active and the novel cationic bacteriostatic sulfoxonium compound, dodecyl methyl benzyl sulfoxonium methosulfate.

EXAMPLE 9

The procedure of Example 8 was repeated using as in the first instance the same gram-positive organism, *Staphylococcus aureus* ATCC 6540. Again, three separate growth control determinations were made; once with a standardized detergent composition, again with the same composition used in Example 8 (except as noted below) in combination with 2% of a compound of this invention, and a third time with the same preparation in combination with 1% of the same new compound.

The active anionic detergent surfactant in the detergent composition of this example, was 17.5% sodium tallow alkyl sulfate in place of the 17.5% sodium tallow alkyl glyceryl sulfonate used in the standardized detergent composition of Example 8. Otherwise the laundering preparation was exactly as in Example 8. For the detergent composition, per se, without the new sulfoxonium cationics, the colony count was about 3500. Using 2% of dodecyl benzyl methyl sulfoxonium methosulfate, the colony count was reduced to about 1380, and at 1% concentrations the colony count was only about 1610.

Thus, compatibility was exhibited between the anionic active of the detergent composition and the cationic sulfoxonium compound with no apparent loss of cleaning power.

Comparable results were obtained against *Escherichia coli* ATCC 26. The standardized washing preparation produced a colony count of 3840, while with 2% by weight of dodecyl methyl benzyl sulfoxonium methosulfate the colony count fell to 1480. An addition of 1%

by weight of the antimicrobial agent produced a colony count of 1960.

EXAMPLE 10

The organic anionic detergent active in the standardized detergent composition in this experiment was 17.5% sodium coconut alkyl sulfate. Against gram-positive *Staphylococcus aureus* ATCC 6538, the detergent composition produced a colony count of 3500. The addition of 2% dodecyl methyl benzyl sulfoxonium methosulfate reduced the count almost in half, to 1890. Surprisingly, somewhat greater improvement was obtained with only 1% of the agent since the colony count was 1720.

Comparable results were obtained against *Escherichia coli* ATCC 26. The figures dropped from an initial count of 3840 to 1790 with 2% additive agent and to 1710 using only 1% additive agent.

The excellent cleaning levels of the standardized cleaning composition were not adversely affected.

EXAMPLE 11

Dimethyl dodecyl amine oxide was employed at 17.5% concentration as a nonionic active in the standardized detergent formulation used in Example 8. The representative compound of this invention remained as dodecyl methyl benzyl sulfoxonium methosulfate. By following the procedure outlined heretofore, the standardized detergent composition resulted in a colony growth of 3500 against gram-positive *Staphylococcus aureus*, ATCC 6538. Addition of 2% dodecyl methyl benzyl sulfoxonium methosulfate reduced the colony growth to 750 and addition of 1% provided a colony count of 770. Both of these figures are markedly low indicating that there was no tendency for the nonionic surfactant in the washing formulation to mask over the bacteriostatic properties of the novel cationic surfactants of this invention. Thus, compatibility exists between the novel cationic sulfoxonium compounds and nonionic surfactants.

Comparable results were obtained against *Escherichia coli* ATCC 26. From an initial colony count of 3560 attained by the model washing formulation, a substantial reduction occurred by the addition of 2% dodecyl methyl benzyl sulfoxonium methosulfate, to a figure of 1710 and by a 1% addition to a figure of 2600.

Several experiments were conducted to determine the behavior of the cationic surfactant sulfoxonium compounds of this invention when combined with other cationic surfactants. The results were positive indicating that such combinations could be made. These experimental results are presented in Example 12 and 13.

EXAMPLE 12

A detergent composition was prepared in which the active was Armeen 16D at 17.5% of the standardized composition in Example 8. Armeen 16D is a cationic surface active agent which is a primary aliphatic amine having as its formula RNH_2 , where R is a normal aliphatic radical derived from naturally occurring fatty acids. Due to a natural raw material source, Armeen 16D contains a mixture of long-chain components. Specifically, the primary amine content of Armeen 16D breaks down to be tetradecyl 13%, hexadecyl 76%, and octadecyl 11.5%. The sulfoxonium compound in this example was dodecyl methyl benzyl sulfoxonium methosulfate and behavior against gram-positive and gram-negative microorganisms was again evaluated.

The detergent composition alone resulted in a colony count of 2520 using *Staphylococcus aureus* ATCC 6538, as compared with a count of 155 obtained when the detergent composition was combined with 2% by weight of dodecyl methyl benzyl sulfoxonium methosulfate. A count of 1320 was obtained with the detergent formulation combined with 1% of dodecyl methyl benzyl sulfoxonium methosulfate.

Against a gram-negative inoculum of *Escherichia coli*

ATCC 26, the basic figure was 3470. With 2% dodecyl methyl benzyl sulfoxonium methosulfate present it was 1960, and with 1% it was also 1960.

EXAMPLE 13

A zwitterionic surfactant compound, 3 (dodecylammonium) propane-1-sulfonate was incorporated as the active surfactant in the standardized detergent composition of Example 8, replacing the 17.5% tallow alkyl glyceryl sulfonate therein. With dodecyl methyl benzyl sulfoxonium methosulfate as the bacteriostatic compound, the series of experiments were duplicated as before, both against both gram-positive and gram-negative organisms.

The basic formulation alone gave a colony count of 2790 when the fabrics were inoculated with *Staphylococcus aureus* ATCC 6538. When 2% dodecyl methyl benzyl sulfoxonium methosulfate was added to the washing formulation, the colony count dropped to only 170. At 1% concentration of dodecyl methyl benzyl sulfoxonium methosulfate, the colony count rose to about 1800, which is still substantially below the figure achieved with the initial standardized formulation in this example.

Comparable results were obtained when the inoculum was gram-negative, *Escherichia coli* ATCC 26. From an initial reading of 2880, the colony counts fell to 1620 and 2040 respectively when 2% and 1% of dodecyl methyl benzyl sulfoxonium methosulfate were included in the washing preparation.

EXAMPLE 14

In this set of experiments an actual commercially available washing formulation was tested, alone and in combination with 2% and 1% of a representative compound of this invention. The result was a product which was perfectly satisfactory in every way.

The washing composition was 17.5% active, 45% sodium dodecyl (tetrapolypropylene) benzene sulfonate and 55% sodium tallow alkyl sulfate, 50% sodium triphosphosphate, 6% sodium silicate, 13.4% sodium sulfate, 10% water and the remainder miscellaneous ingredients such as perfumes, etc.

Used alone against *Staphylococcus aureus* ATCC 6538, it resulted in a colony count of about 3500. When 2% of dodecyl methyl benzyl sulfoxonium methosulfate was added to the washing formulation, the growth of the microorganism was decreased to 1790, only one-half the figure obtained with just the washing formulation.

When a lesser amount, 1% of dodecyl methyl benzyl sulfoxonium methosulfate was employed, the results were still very good, the colony count being about 1840.

The commercial formula used in combination with the representative compounds of this invention retained its superior cleaning level.

Against *Escherichia coli* ATCC 26, the figures obtained were as follows: commercial formula—colony count of 3500; commercial formula +2% dodecyl methyl benzyl sulfoxonium methosulfate—colony count of 1792; and, commercial formula +1% dodecyl methyl benzyl sulfoxonium methosulfate—colony count also of 1790.

Thus, a product is obtained which has the expected high washing level of the commercial formulation coupled with an increased bacteriostatic effectiveness on the laundered fabrics.

EXAMPLE 15

An excellent cleaning composition was obtained by taking another commercial laundering formulation and using it in conjunction with a compound of this invention. The formulation comprised essentially 17.5% sodium dodecyl (tetrapolypropylene) benzene sulfonate, 50% sodium triphosphosphate, 6% sodium silicate, 13.4% sodium sulfate, 10% water and the balance miscellaneous ingredients.

Alone against *Staphylococcus aureus* ATCC 6538, the composition just described yielded a colony count of

about 3500. In conjunction with 2% dodecyl methyl benzyl sulfoxonium methosulfate, the count fell to 900, reflecting excellent control of the growth of the microorganism. In conjunction with only 1% of dodecyl methyl benzyl sulfoxonium methosulfate, the colony count was about 1353, a substantial improvement over the 3500 growth figure scored by the commercial washing formula used alone.

periments are presented below in Table III. Columns I through III present data obtained against *Staphylococcus aureus* ATCC 6538 during tests in which the hexadecyl methyl benzyl sulfoxonium methosulfate was used in amounts of 0%, 2% and 1% based on the weight of the standardized detergent composition. Columns IV through VI relate to data obtained from tests against *Escherichia coli* ATCC 26.

TABLE III

Examples	Surfactant @ 17.5% in Standardized Detergent Composition ¹	I, 0%	II, 2%	III, 1%	IV, 0%	V, 2%	VI, 1%
		Gram-Positive Microorganism ²		Gram-Negative Microorganism ³			
18.....	Tallow AGS (sodium salt).....	3,500	1,876	1,895	3,836	1,820	2,492
19.....	Tallow Alkyl Sulfate (sodium salt).....	3,500	1,437	2,035	3,836	1,904	1,848
20.....	Coconut Alkyl Sulfate (sodium salt).....	3,500	2,343	1,876	3,836	1,932	1,860
21.....	Dodecyl dimethylamine oxide.....	3,500	20	455	3,566	2,408	1,932
22.....	Armeen 16D ⁴	2,520	1,904	2,287	3,472	2,828	2,404
23.....	3 (Dodecyl ammonium) propane-1-sulfonate.....	2,790	1,391	2,268	2,884	2,184	2,426
24.....	Washing preparation of Example 14.....	3,500	2,399	1,792	3,080	2,072	2,100
25.....	Washing preparation of Example 15.....	3,500	1,755	2,137	3,080	2,408	2,548
26.....	Washing preparation of Example 16.....	3,500	2,175	2,259	3,050	2,492	2,128
27.....	Bar soap of Example 17.....	3,500	2,100	2,193	2,720	2,184	2,016

¹ See Examples 8 through 17 for standardized detergent composition used in each instance.
² *Staphylococcus aureus* ATCC 6538.
³ *Escherichia coli* ATCC 26.
⁴ See Example 12 for identification.

EXAMPLE 16

A product comprising 14% sodium dodecyl (tetrapolypropylene) benzene sulfonate, 47.7% sodium tripolyphosphate, 19.1% sodium sulfate, 9.7% sodium silicate, 1.6% sodium toluene sulfonate, and the remainder miscellaneous ingredients was used in these experiments. Fabric swatches washed in this formula showed a *Staphylococcus aureus* ATCC 6540 growth of about 3500. A 2% addition of dodecyl methyl benzyl sulfoxonium methosulfate to the formula resulted in only 840 colonies growing after the incubation period. A 1% addition had the effect of limiting colony growth to 1230. In all instances the cleaning power of the product remained at its designed level.

EXAMPLE 17

The tests were also extended to bar soap formulations to determine the usefulness in such cases. The results were excellent. No problems were encountered in using bar soap formulations along with the compounds of this invention. The exceptional mildness of these compounds is another advantage which they lend to such a formulation.

In this instance, a milled toilet soap comprising 83.5% of an 80% tallow: 20% coconut sodium soap, 13.0% volatiles, 2.0% unsaponifiables, and the remaining minor amounts of miscellaneous ingredients, was used as a bar soap formula.

The same procedure as used in each of the other examples was followed. That is a .25% concentration of this bar formula was prepared and the test swatches were laundered therein, inoculated with *Staphylococcus*, incubated and a colony count made. This gave a colony count of about 3500.

After the bar washing formulation was modified to include 2% dodecyl methyl benzyl sulfoxonium methosulfate, the colony count was down to 1920.

A third was using only 1% of dodecyl methyl benzyl sulfoxonium methosulfate was run. The count was 1860, essentially the same as in the instance when 2% was employed.

Examples 8 through 17 were repeated in almost identical fashion. The only variation was that a different member of the new series of sulfoxonium compounds was selected, namely, hexadecyl methyl benzyl sulfoxonium methosulfate. The Quinn procedure discussed immediately preceding Examples 8 through 17 was followed explicitly.

The data that were obtained from these additional ex-

This table shows that the combination of hexadecyl methyl benzyl sulfoxonium methosulfate with other organic synthetic detergent surfactants presented no problems of incompatibility. In no instance was the bacteriostatic effectiveness of the representative sulfoxonium compound of this invention masked over or destroyed. An improvement was obtained in each instance due to the ability of the hexadecyl methyl benzyl sulfoxonium methosulfate to control the growth of both gram-positive and gram-negative organisms even in the presence of the various types of organic surfactants.

The compounds of this invention including those prepared by Examples I through VII, can be employed in all types of detergent compositions, as for example, liquid, bar or granular compositions. Such detergents may contain varying amounts of these new compounds but generally there can be present from 1% to about 20% of the new compounds per total weight of the detergent composition. Preferably, there should be present from 2 to 10% of a compound of this invention in order to receive the maximum effect of the unique blend of properties.

There is thus provided by this invention improved cleansing and washing compositions for laundry and personal use comprising active detergent compounds and an effective amount of at least one of the compounds of this invention.

The unusual and unexpected combination of properties possessed by these compounds suggests many other ramified uses. For example, the following can be mentioned: the inclusion of these new surfactant compounds in cosmetic compositions such as organic cleansing detergent preparations, shaving creams, shaving soaps, shampoos, ointments, facial creams and the like. As a consequence, these materials would be of improved quality, being rendered more highly antiseptic due to the bacteriostatic effectiveness of the novel sulfoxonium compounds.

In such compositions, of course, various colors, antioxidants, perfume, water softeners, and other materials can be used without affecting the desirable properties of the new class of sulfoxonium surfactant materials.

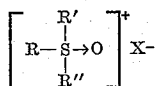
The foregoing description of the invention has been presented describing certain operable and preferred embodiments. It is not intended that the invention should be so limited since variations and modifications thereof will be obvious to those skilled in the art, all of which are within the spirit and scope of this invention.

What is claimed is:

1. High molecular weight sulfur-containing cationic

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surface active compounds corresponding to the following structural formula:



wherein

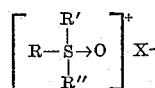
R is selected from the group consisting of alkyl and alkenyl radicals containing from 10 to 20 carbon atoms,

R' and R'' each are selected from the group consisting of lower alkyl, benzyl, chlorinated benzyl, and alkyl-benzyl wherein the alkyl substituent contains from 1 to about 4 carbon atoms,

and wherein

X represents an anionic substituent.

2. Sulfoxonium compounds having a structural formula corresponding to:



wherein

R is an alkyl radical containing from 12 to 18 carbon atoms,

R' and R'' each are selected from the group consisting of lower alkyl, benzyl, chlorinated benzyl, and alkyl

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benzyl wherein the alkyl substituent contains from 1 to about 4 carbon atoms,

and wherein

5 X represents an anionic substituent selected from the group consisting of halide, sulfate, methosulfate, p-toluene sulfonate and nitrate radicals.

3. Dodecyl dimethyl sulfoxonium methosulfate.

4. Tetradecyl dimethyl sulfoxonium methosulfate.

5. Hexadecyl dimethyl sulfoxonium methosulfate.

6. Dodecyl methyl benzyl sulfoxonium methosulfate.

7. Dodecyl methyl o-chlorobenzyl sulfoxonium methosulfate.

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