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AEROSOL GERMICIDAL COMPOSITIONS

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This application is a continuation-in-part of my application Serial No. 437,313 filed March 4, 1965, and now abandoned.

The present invention relates to two-phase, self-propellant compositions. More particularly, this invention is directed to novel pressurized germicidal compositions.

The necessity for prophylactic germicidal action has recently become of major importance, particularly because of the ineffectiveness of antibiotics to offer continued therapeutic protection against many of the common bacteria and particularly the coagulase-positive *Staphylococcus aureus*. The compositions of the present invention provide multi-germicidal action in that they can be used as surface disinfectants and/or air sanitizers while also performing effectively as deodorizers. An aerosol germicidal composition which can simultaneously disinfect surfaces, sanitize the air, and deodorize the air in one simple operation is a novel and revolutionary concept in pressurized household disinfectants.

It has been established through market research surveys that the concept of a multi-purpose pressurized germicide is particularly attractive to the consumer. However, the reduction of this concept to a reliable, effective product suitable for consumer consumption required years of research and development. To provide a pressurized product which could function as a surface spray and a space spray in one operation without resorting to elaborate dual valving assemblies and the like required a sharp break with traditional aerosol formulating and packaging concepts.

It has further been established that a significant percentage of the consumers in the U.S. today do not consistently shake or agitate a pressure package prior to using it. Accordingly, if it were necessary to shake an aerosol germicidal composition prior to discharge, a significant percentage of the consumer market would be misusing such a product. Such misuse with a conventional pressurized composition, such as a cleaner or polish, although unsatisfactory would be tolerable; however, it would be wholly unacceptable with an aerosol germicidal composition. Therefore, it is essential that the aerosol germicidal compositions of the invention be capable of being dispersed without resorting to agitation.

It has been further established that under normal use conditions commercially available aerosol germicides have a history of intermittent use resulting in prolonged shelf life, i.e., up to 18 months and longer. Accordingly, the usual problem areas relating to shelf life which are common to most pressurized products become exaggerated with aerosol germicides. The most significant of these problem areas are product stability and corrosion. Of course, the presence of water and quaternary substances which are required for the compositions of the present invention further adversely influence the corrosion and stability properties of such a composition.

By definition a surface disinfectant is required to leave a treated surface free from disease-producing germs, and to destroy 100% of the vegetative, non-spore-forming bacterial cells. In contrast, a sanitizing composition is required to destroy something less than 100% of the germs present, usually at least about 90%.

The official disinfectant test for pressurized surface sprays has been established by the Association of Official

Agriculture Chemists and the compositions of the invention qualify as disinfectants under this test. Prior to registration as a surface disinfectant the United States Department of Agriculture requires that all commercially available compositions to be so used pass this test, utilizing the label instructions on the product container. Two types of bacteria are used for this test. They are *Staphyloccus aureus* (ATCC 6538) and *Salmonella choleraesuis* (ATCC 10708). The test procedure is described in detail in the Journal of the Association of Official Agriculture Chemists, vol. 44, No. 1, pp. 137–138 (1961). There is also a brief description of this test infra. In addition to the foregoing for the purposes of the present invention, a surface disinfectant is defined as a composition capable of residual anti-germ action against these tests organisms. This residual activity has been observed to be at least 90% effective for a minimum of 30 days when applied to a series of contaminated surfaces which are maintained under controlled conditions. These compositions are applied in a concentration sufficient to thoroughly wet the surface.

For the purposes of the present invention an air sanitizing composition is defined as a composition which will produce a reduction in air-borne bacteria, in a specifically defined enclosed test area, of at least 90% under the air sanitizing test procedure described in detail below.

The use of pressurized spray formulations to sanitize air in enclosed spaces is known in the art. However, heretofore these formulations usually contained glycols such as triethylene glycol which have been accepted in the art as one of the most effective air sanitizers. Until recently, it has been generally accepted in the art that an effective air sanitizing formulation would have to contain a glycol. Glycols, however, are not generally considered satisfactory for use in surface disinfecting compositions in that they leave a sticky film residue on surfaces sprayed. Accordingly, a multi-purpose aerosol germicidal composition, such as described in the present invention, would preferably not contain substances which leave unsightly residues on treated surfaces including glycols. In a particularly preferred embodiment of the invention the aerosol compositions are substantially glycol-free.

It should be understood that, in addition to the various active ingredients present in the compositions of the invention, the nature of the spray produced is critical to satisfactory performance as a surface disinfectant-air sanitizing composition. For example, if the spray produced approaches a true aerosol, i.e., a fine mist-like spray in which 80% of the particles are less than 30 microns in diameter and none are over 50 microns in diameter, an exceptionally good air sanitizing spray would result. However, excessive particle bounce-off and ineffective wetting of surfaces would be obtained during the normal spray cycle so that the pressurized product would not be suitable for use as a surface spray. On the other hand, if the spray produced approaches a surface spray, i.e., wherein a substantial amount of the composition is consistently discharged as relatively large particles which rain out and wet the surface of the area being sprayed without charging the air, the pressurized product would probably be effective as a surface disinfectant but would not be satisfactory for use as an air sanitizer. Accordingly, in the absence of a dual valve mechanism, a suitable surface disinfecting-air sanitizing composition has a spray pattern which is a compromise between a true aerosol spray and a surface spray. Moreover, it is critical to the germicidal properties of the compositions of the invention that this type of spray be maintained throughout the life of the pressurized product.

The compositions of the invention can be described as two phase, pressurized surface disinfectant and air sani-

tizing compositions comprising a gaseous phase and a stable homogeneous liquid phase wherein the liquid phase contains:

(a) At least about 10% by weight water,

(b) At least about 15% by weight of a normally gaseous halogenated hydrocarbon propellant,

(c) Ethanol in a concentration sufficient to form a homogeneous solution with the water and propellant present,

(d) At least 0.05% by weight of a mixture of certain quaternary compounds, and

(e) An amphoteric surfactant which is compatible with the germicidal properties of the mixture of quaternary compounds.

The halogenated hydrocarbon propellant referred to above is a normally gaseous liquid, that is, a substance which is gaseous at standard atmospheric conditions, but liquid under moderate pressure. Therefore, the gaseous phase of the composition comprises as the major ingredient vapors of the propellant and in addition may contain vapors from other components of the liquid phase such as ethanol vapors. However, the primary propelling force arises from vaporization of the propellant.

The two phase compositions of the invention are hermetically sealed in a container having a suitable valve assembly for venting the pressurized systems to the atmosphere. The valve is usually hand operated and carries a dip tube extending into the liquid phase. In its most simple form the valve will have two orifices which are open substantially at the same time by moving a suitable button. One orifice opens to the dip tube and the other to the atmosphere. The valve assembly is discussed further below. On actuation of the valve, pressure arising from the vaporization of the propellant forces the liquid phase up the dip tube and into the atmosphere. When the propellant reaches the atmosphere, it vaporizes practically instantly and with almost explosive force, thus breaking up the liquid stream into a large number of small droplets. It has been found that the surface disinfectant-air sanitizing performance of the compositions of the invention is dependent at least in part upon the size of these droplets which are in turn controlled by the amount and type of propellant used, the presence of a homogeneous liquid phase, and the valving employed.

It has been found that if the composition of the two phases of the pressurized surface disinfectant air sanitizer remains substantially constant until the pressure package is exhausted, effective surface disinfecting and air sanitizing is consistently obtained. In order to assure that the ratio of the various components, particularly in the liquid phase, remains substantially constant over the useful life of the product, it is essential to avoid disproportionate discharge of these components. Accordingly, it is essential that the liquid phase remains a homogeneous solution and that the total discharge of the container be drawn directly from said liquid phase. Thus, except for equilibrium with the liquid phase, the composition of the gaseous phase remains essentially static during the life of the product and functions primarily as a head of pressure forcing the liquid phase from the pressure package. Therefore, the use of valve assemblies which draw product from the gaseous phase for discharging, i.e., vapor tap valves, is preferably avoided. It has been found that when a vapor tap valve is employed with the compositions of the invention, the propellant and the ethanol are discharged at a disproportionate rate eventually causing the formation of two liquid phases and/or adversely effecting the spray characteristics and/or germicidal performance of the product.

The self-propellant compositions of the invention have been found to destroy odors by killing the bacteria which produce them. In addition, the compositions of the invention have been found to prevent mold, mildew, and rot while leaving a clean, pleasant odor without the strong disinfectant odor common to most disinfectant compositions. Prior to describing the germicidal properties of the compositions of the invention a detailed description of these compositions and particularly the various components thereof appears warranted.

(a) *Water.*—It has unexpectedly been found that the surface disinfecting-air sanitizing properties of the compositions of the present invention are dependent upon the presence of water. That is, when water is excluded from the composition of the invention, the resulting compostion fails the surface disinfecting and air sanitizing tests described below. (See Example 15.) It has been observed that water must comprise at least about 10% by weight of the composition in order to achieve the required anti-microbial activity specified for an air sanitizing composition. (See Examples 2–14.) For example, it has been discovered that about 7.5% by weight water failed to provide satisfactory surface disinfecting and air sanitizing activity. (See Table 1.) The concentration of water in the compositions of the invention can be as high as 25% by weight; however, this upper limit is not controlled primarily by anti-germ action but rather by the effect such higher concentrations of water have on maintaining a homogeneous liquid phase, and the spray characteristics of the pressurized composition. The criticality of water in the compositions of the invention is described and illustrated vividly in Examples 2–6 and 15 infra.

(b) *Propellant.*—The discharge of the liquid phase is chiefly effected by means of the presence therein of a normally gaseous halogenated hydrocarbon propellant. Suitable propellants for the compositions of the present invention are halogenated derivatives of the hydrocarbon gases and it is this replacement of hydrogen atoms by chlorine and especially fluorine atoms that gives them their unique application in the compositions of the invention. The halogenated propellants are stable, colorless, non-flammable, essentially non-toxic and noncorrosive to common pressure package fabrication materials. Hydrolysis rates of fluorinated substances are exceptionally low, much lower than the rates of nonfluorinated halogen derivatives of hydrocarbon gases. Unlike nonliquefied propellants where the pressure in the container drops as the product is discharged, the halogenated hydrocarbon propellants provide a substantially constant pressure throughout the useful life of the product.

The flammability determination of a pressurized product is a prime factor in establishing the shipping classification and appropriate packaging restrictions for movement through interstate commerce. The flammability property of a product is also required for additional compliance with regulatory codes on local levels, and to provide essential statements of caution for insertion on the container label to adequately protect the potential consumer in the event of product misuse. Under current ICC shipping regulations ethanol-containing pressurized compositions such as those defined by the instant invention could not be shipped in interstate commerce if they were pressurized with most hydrocarbon propellants. Moreover, under certain conditions the use of a hydrocarbon propellant exclusively has been found to produce a coarse spray which is unsatisfactory for air sanitizing purposes. Therefore, at least a major amount by weight of the propellant used in the invention will be a halogenated hydrocarbon propellant. In a preferred embodiment of the invention all of the propellant will be a halogenated hydrocarbon propellant.

The normally gaseous halogenated hydrocarbon propellants useful in the compositions of the invention may be represented by the structural formula:

$$C_nH_xCl_yF_z \qquad (I)$$

wherein n is a whole number from 1 to 2, x is a whole number from 0 to 4, y is a whole number from 0 to 3, and z is a whole number from 1 to 4, and the sum of x, y, and z is equal to $2n+2$, with the proviso that when n equals 1, y is at least 1. Examples of suitable propellants in-

clude monochlorotrifluoromethane, trichloromonofluoromethane, dichlorodifluoromethane, dichloromonofluoromethane, monochlorodifluoromethane, trichlorotrifluoroethane, dichlorotetrafluoroethane, difluoroethane, and difluoromonochloroethane. This structural formula shall be referred to hereinafter as Formula I.

The concentration of propellant present in the composition of the invention dictates in part the amount of water that can be present and the amount of ethanol necessary to produce a homogeneous liquid phase. As noted above, the concentration of propellant controls the spray characteristics and ultimately at least in part the surface disinfecting-air sanitizing properties of the composition. It has been found that propellant in a concentration of at least about 15% by weight of the total composition must be employed in order to obtain marginal air sanitizing performance. (See Example 13.) Although propellant concentrations higher than about 30% by weight can be employed, it has been observed that the surface disinfecting properties are not optimum at propellant concentrations as high as from about 35% to about 50% by weight. (See Examples 11 and 10 respectively.) It is interesting to note however, that at 50% by weight propellant satisfactory air sanitizing activity was obtained.

An additional consideration which limits the maximum concentration of propellant in the compositions of the invention is the requirement that the liquid phase remain a homogeneous liquid, i.e., the solubility of the ethanol/water solution cannot be exceeded. In this regard it should be noted that the ratio of propellant to water in the composition of the invention can range from about 3:1 to about 1:1. In a preferred embodiment the ratio of propellant to water is from about 2.5:1 to about 1.5:1.

One further limitation on maximum propellant concentration acceptable in the compositions of the invention is the internal pressure allowable in these formulations as dictated by various federal and local shipping regulations. The boiling points of the propellants useful in the compositions of the invention are generally lower than normal room temperature at one atmosphere. Accordingly, it is preferable that the compositions of the invention produce vapor pressures no greater than about 60 p.s.i.g. at 21° C.

It is understood that a suitable propellant may be either a single propellant selected from the propellants described in Formula I above or a compatible admixture of these substances, providing said mixture has a suitable boiling point. It is further understood that the propellant is totally soluble in the ethanol/water preparation to be dispensed and that the total ethanol/water/propellant solution has a vapor pressure less than about 60 p.s.i.g. at 21° C. Some of the propellant compounds described above such as trichloromonofluoromethane and trichlorotrifluoroethane boil at temperatures higher than about 21° C. at a pressure of one atmosphere and thus, when used alone, would not be practical as propellants in the compositions of the invention particularly in climates where normal room temperatures at which the compositions are to be dispensed are below their boiling points. However, these halogenated hydrocarbons are useful in propellant mixtures where they can be utilized as pressure diluents for those propellant compounds which have lower boiling points and correspondingly higher pressures. It has been observed that reducing the amount of propellant by increasing the water content of the ethanol medium, while limiting the propellant to that quantity which will go into solution in the water-containing ethanol solution, does not materially alter the internal pressure of the package. Increased amounts of water with an attendant decrease in the amount of propellant in the ethanol/water/propellant solution will at most cause a decrease in the internal pressure within the package of only a few p.s.i.g.

(c) *Ethanol.*—It has been established that ethanol is the only readily available organic solvent suitable as a cosolvent for the Formula I propellants and water in the compositions of the present invention. That is, ethanol has adequate solubility for the germicide and surface active agent and the alcohol/water solutions used are sufficiently miscible with the Formula I propellants to provide a homogeneous liquid phase. In this regard it should be understood that the greater the water content, the lesser the amount of the particular propellant selected from the Formula I propellants which will go into solution in the ethanol/water medium. In addition to its function as a coupling agent or cosolvent for the water and propellant, ethanol functions as a non-toxic disinfectant and thereby contributes substantially to the surface disinfecting properties of the composition of the invention. Other organic solvents which display adequate cosolvent capabilities have been found to be too toxic to be useful in air sanitizing applications, such as methanol, and/or not sufficiently effective as disinfectants to assist in obtaining the surface disinfectant results achieved with the compositions of the invention. A further advantage of employing ethanol as the cosolvent is its odor, which is particularly pleasing when compared with that of other lower aliphatic alcohols such as isopropanol and butanol most of which require the addition of masking agents. It is essential to optimum performance of the compositions of the invention that the cosolvent employed be sufficiently volatile so that it does not leave a residue on treated surfaces.

The concentration of ethanol suitable for the compositions of the invention as noted above is controlled at least in part by the solubilizing function of the ethanol. However, it has been found that the germicidal properties of the compositions of the invention are also dependent upon the concentration of the ethanol present. In this respect it has been found that the concentration of ethanol should be from about 50% by weight to about 70% by weight of the composition. In a particularly preferred embodiment the ethanol comprises from about 60 to about 65% by weight of the composition.

LIQUID PHASE

It is essential to the proper performance of the compositions of the invention that the liquid phase be a stable homogeneous liquid solution throughout the life of the product. That is, in order to obtain consistent surface disinfecting and air sanitizing performance over the life of the product, it has been found necessary that the product to be dispensed be drawn only from the liquid phase and that the composition of the liquid phase remain substantially constant. It has been found that only by this approach can the spray pattern, the chemical composition and ultimately the germicidal properties of the product be effectively controlled. Thus, the use of vapor tap valve assemblies are avoided and the compositions are formulated so that the liquid phase does not undergo layering, i.e., separation into two or more liquid phases under various environmental conditions.

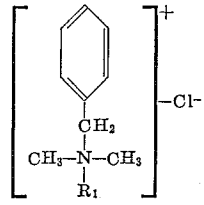
With respect to stability, certain compositions of the invention have been stored in glass pressure packages at temperatures as low as about —39° F. for extended periods with no evidence of phase formation and/or precipitation. In addition to being free from the formation of separate liquid layers the compositions of the invention have the property of being able to resist substantial corrosion of the pressure package. Heretofore, in order to obtain satisfactory corrosion resistance with water containing compositions and particularly those compositions having the pH characteristic of quaternaries it has been necessary to include substantial amounts of corrosion inhibitors, emulsify the water in water-in-oil emulsion and/or provide the container with a heavy duty, costly liner.

The unique resistance to corrosion characteristic of the compositions of the invention and the role the surfactant unexpectedly plays in this respect is described in detail in Example 16. It should be understood that germicidal

compositions stored in containers which are substantially free from corrosion have been found to be more effective with respect to providing consistent anti-germ activity over the life of the product. This improved anti-germ activity is thought to be due at least in part to the absence of corrosion by-products which interfere with the cidal activity of the active ingredients such as the quaternaries.

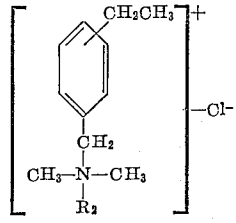
(d) *Quaternary.*—Although a vast array of germicides are available commercially today including numerous quaternary compounds the compositions of the invention are limited to a specific class of quaternary compounds described in detail below. These compounds are unexpectedly well suited for use in the surface disinfecting-air sanitizing compositions of the invention by reason of their preeminent bactericidal properties. These quaternaries have been found to provide unobvious and unexpected surface disinfecting and air sanitizing performance when used in the compositions of the invention.

These quaternary compounds comprise a mixture of two classes of compounds. The first class of compounds can be represented structurally as:



(II)

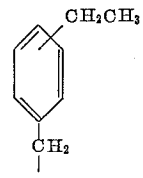
wherein R_1 represents a mixture of n-alkyl groups comprising a major amount of C_{14} a lesser amount of C_{16} and minor amounts of C_{12} and C_{18} alkyl groups. The foregoing shall be referred to hereinafter as Formula II. The second class of quaternary compounds can be represented structurally as:



(III)

wherein R_2 represents a mixture of n-alkyl groups comprising a major amount of C_{12} lesser amounts of C_{14} and C_{16} and a minor amount of C_{18} alkyl groups. The foregoing shall be referred to hereinafter as Formula III. These Formula II and III compounds can be described broadly as n-alkyl dimethyl benzyl ammonium chlorides and n-alkyl dimethyl ethylbenzyl ammonium chlorides respectively.

The C_{14} portion of the n-alkyl group in the Formula II quaternary is recognized as the most bacteriologically active n-alkyl component of the Formula II compound. Whereas, the ethylbenzyl group, i.e.,



of the Formula II class of quaternaries increases the germicidal potency of the basic structure severalfold and widens the effective pH range of the germicide from the highly acid to the highly alkaline. The pH of the compositions of the invention ranges from about 9 to about 11 and is usually 10 or slightly greater.

In a preferred embodiment of the invention the Formula II class of compounds has approximately the following composition: R_1 represents a mixture of n-alkyl groups comprising from about 55% to about 65% C_{14}, from about 25% to about 35% C_{16}, from about 2% to about 8% C_{12} and from about 2% to about 8% C_{18}; and the Formula III class of compounds has approximately the following compositions: R_2 represents a mixture of n-alkyl groups comprising from about 45% to about 55% C_{12}, from about 25% to about 35% C_{14}, from about 12% to about 22% C_{16} and from about 1% to about 8% C_{18}.

In a particularly preferred embodiment of the invention the Formula II and Formula III classes of compounds have approximately the following compositions: R_1 in Formula II represents a mixture of n-alkyl groups comprising about 60% C_{14}, about 30% C_{16}, about 5% C_{12}, and about 5% C_{18}, and R_2 in Formula III represents a mixture of n-alkyl groups comprising about 50% C_{12}, about 30% C_{14}, about 17% C_{16} and about 3% C_{18}. These compositions will be referred to hereinafter as Formulas II(a) and III(a) respectively.

When the quaternaries defined by Formulas II and III are combined in a ratio of about 1:2 to about 2:1 unexpected and unobvious synergistic microbiological action is noted. In a particularly preferred embodiment of the invention the ratio of Formula II to Formula III quaternaries present in the composition is about 1:1.

It has been found that these mixtures of the Formula II and III quaternaries provide higher phenol coefficients than one can usually obtain with commercially available germicides, i.e., over 900 vs. *S. aureus* (American Type Culture 6538) and over 600 vs. *S. typhosa* (American Type Culture 6539), thus providing a greater reserve of killing power which is essential in providing the residual disinfectant properties of the claimed compositions. Of course, with minimum phenol coefficient values of this magnitude it is readily apparent that compositions containing these quaternaries will have correspondingly high dilution factors.

Mixtures of the Formula II and III quaternaries have a high hard water tolerance level thereby avoiding the need for deionized water in formulating the compositions of the invention. However, an even more significant advantage of the high hard water tolerance level of these compounds is the increased rate of germ kill. That is, salts which are commonly present in hard water are known to interfere with the germicidal properties of most germicides and particularly quaternaries and accordingly reduce the rate of germicidal kill. However, the Formula II and III compounds are surprisingly effective under hard water conditions and are known to produce a high rate of germ kill under hard water conditions even under short periods of exposure.

Mixtures of the Formula II and III quaternaries are stable, non-volatile substances unaffected by freezing, high temperatures, pH or flammable solvents such as ethanol. Moreover, these mixtures of quaternaries display surface active properties and possess strong wetting action. Accordingly, these substances assist in effectively wetting surfaces, penetrating cracks, crevices and other surface irregularities and thereby contribute substantially to the surface disinfecting activity of the compositions of the invention. Moreover, the substantially non-volatile nature of these substances contributes significantly to the residual disinfecting properties of these compositions of the invention. Therefore these quaternaries will wet and penetrate treated surfaces effectively and remain as an effective antimicrobial agent on the surface for prolonged periods of time after the more volatile components have vaporized.

Within certain concentration limitations these mixtures of quaternaries are compatible with certain amphoteric surfactants. However, these substances are generally incompatible with anionic surfactants.

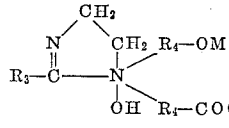
It has been established that effective surface disinfecting and air sanitizing can be obtained with 1:1 mixtures of the Formula II and III quaternaries where the total germicide concentration in the compositions of the invention is

as low as 0.050% by weight. A detailed description of the experiments conducted to determine minimum effective concentrations of these substances is set forth in Examples 6–14. The maximum concentration of germicide that can be used in the compositions of the invention is controlled in part by economic considerations, i.e., above about 0.8% by weight total germicide the addition of more quaternary does not produce any noticeable enhancement of anti-germ activity. The relationship between the Formula II and III quaternaries and the surfactants useful in the compositions of the invention is discussed in detail below.

The Formula II and III compounds can be prepared according to the various methods described for related compounds in U.S. Patent 2,676,986 to Wakeman et al. That is, mixing the appropriate modified benzyl chloride with various n-alkyl dimethyl amines until the reaction becomes exothermic has been found to be a particularly effective method for producing these substances.

(e) *Surfactant.*—Although the Formula II and III quaternary compounds function as surface active agents it has been found necessary in order to obtain consistent surface disinfectant performance with the compositions of the invention and optimum stability, particularly with respect to corrosion, that a compatible, stable, amphoteric surfactant must be present in the compositions of the invention. It was found that a compatible surfactant provides a more effective wetting of the contaminated surface and also contributes to the corrosion resistance of the composition while excessive residue on treated surfaces is avoided.

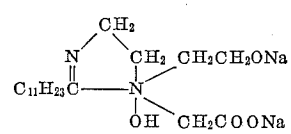
Suitable amphoteric surfactants include certain metal salts and certain salt free substituted quaternary hydroxy cycloimidinic acid metal alcoholates such as disclosed in U.S. Patents 2,528,378, 2,773,068, and 2,781,354 to Mannheimer. These compounds can be represented by the following structural formula:



(IV)

wherein R_3 represents a hydrocarbon radical having from about 4 to about 18 carbon atoms, R_4 represents various aliphatic hydrocarbons and oxygenated aliphatic hydrocarbon groups including: (1) aliphatic hydrocarbon groups having from 1 to 4 carbon atoms, (2) hydroxy substituted hydrocarbon groups having from 1 to 4 carbon atoms, (3) aliphatic ether groups, having from 2 to 4 carbon atoms with each of said groups having a single ether linkage therein, (4) aliphatic hydroxy substituted ether groups having from 2 to 4 carbon atoms, (5) aliphatic keto groups containing from 2 to 4 carbon atoms and (6) aliphatic hydroxy substituted keto groups having from 2 to 4 carbon atoms; and M represents an alkali metal such as potassium or sodium or a hydrogen atom. The foregoing will be referred to hereinafter as Formula IV.

The surfactant for use in a preferred embodiment of the invention is a metal salt of a substituted quaternary hydroxy cycloimidinic acid alcoholate having the structural formula:



(V)

The foregoing will be referred to hereinafter as Formula V.

In general the Formula IV surfactants have the following outstanding features, they are: non-toxic, completely biodegradable; nonirritating to skin and eyes and thus can be used in air sanitizing compositions; stable to acid, alkali, and hard water conditions; compatible with the Formula II and III quaternaries and germicidally active.

The Formula IV surfactants are ionically balanced amphoteric substances which in part contributes to this unique compatibility with the Formula II and III quaternaries. This ionic balance is particularly advantageous to the compositions of the present invention in that due to its total compatibility with cationic and anionic substances the formation of insoluble reaction products is avoided. The method of preparing the Formula V compounds is described in the U.S. patents to Mannheimer referenced above.

In addition to its compatibility with the Formula II and III quaternaries the Formula IV surfactants have been found to provide unexpected and unobvious corrosion resistance to the compositions of the invention. For example, the pressure package corrosion studies and the influence of the Formula V surfactant thereon are described in detail in Example 16.

The Formula IV and particularly the Formula V surfactants have been shown to be effective in the compositions of the invention at concentrations as low as about 0.05% by weight. Concentrations substantially greater than about 1.0% by weight have been found to provide little additional benefit to the germicidal performance of the compositions of the invention. In a preferred embodiment of the invention the Formula V surfactant will comprise about 0.1% by weight of the composition. The ratio of surfactant to the Formula II/Formula III mixture of quaternaries is preferably maintained between from about 1:1 to about 1:3.

If a metallic aerosol container is used, it is preferable to add a small portion of a suitable corrosion inhibitor to the composition. For example, a corrosion inhibitor in a concentration from about 0.01 to about 0.2% by weight of the total composition has been found desirable under certain conditions. Typical corrosion inhibitors include oleic acid, N-fatty beta-aminopropionate, N-fatty beta-aminodipropionate, hexynol, morpholine, formaldehyde, 2-hydroxypropylamine nitrite, mixtures of propylene glycol and sodium nitrite. The latter compositions are particularly preferred, i.e., 2-hydroxypropylamine nitrite and mixtures of propylene glycol and sodium nitrite, since they are compatible with the Formula II and III quaternaries and the Formula IV surfactants under substantially all conditions.

Depending on the nature of the product desired the compositions of the invention may contain various additives which are soluble therein including perfumes, quaternary masking agents such as isopropyl myristate and medicinal substances such as ethers, menthol and camphor.

The production of the compositions of the invention may, for example, be effected by dissolving the Formula II and III quaternaries, the Formula IV surfactant and any additional substances such as corrosion inhibitors, perfume and the like in the ethanol. The appropriate concentration of water is added with agitation. The resultant intermediate is then introduced into a pressure container and the normally gaseous halogenated hydrocarbon Formula I propellant is introduced by conventional aerosol filling techniques such as the under-the-cap filling method. It is preferable to provide for less than 20% by volume head space when filling the pressure package. In a particularly preferred embodiment 10% by volume of the container will comprise the head space.

As noted above, the practice of this invention contemplates the use of a conventional valve with a mechanical break-up button. Both of these are standard and well known in the art. The valve which is sealed in the container to produce a closed system has a series of orifices. The first is a body orifice which is in cooperative engagement with a dip tube so that the liquid phase coming up the dip tube passes through the body orifice. The second orifice is referred to as a stem orifice which communicates with the body orifice and

also with the exit orifice of the valve. The latter communicates with the atmosphere by means of a mechanical break-up button.

Referring now to the size of the various orifices, the body orifice may be from about 0.010 to about 0.100 inch in diameter. The stem orifice may be from about 0.01 to about 0.08 inch in diameter. The mechanical break-up button may be from about 0.012 to about 0.025 inch in diameter. Obviously, a fair degree of latitude is possible in the valving of a container for use with the compositions of this invention. It should be noted that since the liquid phase is homogeneous, a capillary dip tube is not required; accordingly dip tubes having inside diameters as large as about 0.180 inch can be used.

SURFACE DISINFECTANT TEST

In the AOAC disinfectant test referenced above, the test organisms employed are *Salmonella choleraesuis* (ATCC 10708) and *Staphylococcus aureus* (ATCC 6538) to which have been added 0.02 ml. of octylphenoxypolyethoxyethanol per 10 ml. suspension of each test organism.

Individual 48 hour-nutrient broth cultures of the above described test organisms are thoroughly shaken and allowed to settle for 10 minutes. With a sterile 4.0 mm. loop, 0.01 ml. of the test culture is spread over a one square inch marked area of a 1" x 3" microscopic slide which slide is contained in a petri dish. A cover is immediately placed over the petri dish and this operation is repeated until 30 slides have been prepared for each organism. All slides are dried for about 30 minutes at about 37° C.

Ten of the thirty slides for each test organism are selected at random and each is sprayed for about 3 to 5 seconds at a distance of about 6 to about 4 inches with the composition of the invention. (See Example 1.) After spraying, each slide is held for 10 minutes. The excess liquid is drained off, and the slide is then transferred with flamed forceps to a 32 x 200 mm. bacteriological tube containing a subculture medium. The subculture medium employed is described in detail in the AOAC reference cited above.

Ten additional slides of *Staph. aureus* are selected at random. Each slide is sprayed for 5 seconds at a distance of 3 to 4 inches with a 2% by weight distilled water solution of phenol using a De Vilbiss atomizer No. 251. These treated slides are held for 10 minutes, drained and transferred to the subculture medium in the same manner described above. Ten slides of *S. choleraesuis* are treated in the same manner using a 1.5% by weight distilled solution of phenol. Each of the remaining 10 slides of *Staph. aureus* is treated in this manner using a 1.25% by weight distilled water solution of phenol. Each of the remaining 10 slides of *S. choleraesuis* is treated in a similar manner with a 0.5% by weight distilled water solution of phenol.

All the test tubes are incubated for 48 hours at 37° C. The results are read as growth, (+), or no growth, (−). Thus, killing all test organisms in 10 out of 10 trials would read 0+, and 9 out of 10 would read 1+, and so forth.

AIR SANITIZING TEST

The air sanitizing test utilized to establish the air sanitizing properties of the compositions of the invention has been developed specifically for these compositions. This is an in vivo test which has been designed to parallel as closely as possible actual use conditions.

The test organisms employed in this test are 24 to 48 hour cultures of *Staphylococcus lysodeikticus* and *Escherichia coli* on nutrient agar. A portion of each test culture is dispersed in 10 ml. of A.O.A.C. "PC" broth. One ml. of the resultant test organism dispersion is transferred to a nebulizing container.

A petri dish containing from about 70 to about 80 ml. of "2×Letheen agar" (the standard A.O.A.C. formula which is modified so that it contains twice the weight of lecithin and polyoxyethylene sorbitan monooleate normally required) is placed in a Reyniers air slit sampler equipped with a rotating one-hour timer mechanism.

The air slit sampler containing the petri dish is placed in the center of a "Peet-Grady" test chamber. The rotating clock mechanism is actuated thereby rotating the petri dish agar surface under the slit in the air sampler. At this time an air jet is employed to distribute 1 ml. of the test organism dispersion throughout the test chamber. The air jet assembly is equipped with a needle-valve capillary tube attached to a 1 ml. nebulizing container which holds the test organism dispersion.

Fifteen minutes after the test organism dispersion is introduced into the test chamber a composition of the invention (see Example 1) is discharged into the test chamber at a rate of one second per 100 cubic feet. The air sampler continues rotating for the remainder of the one hour period. At the end of this time the petri dish is removed from the air sampler and incubated for about 48 hours at about 30° C. (for *S. lysodeikticus*) and at about 37° C. (for *E. coli*). The Petri dish can then be compared with a control, i.e., one treated in the same manner except that the composition of the invention was not introduced into the test chamber during the one hour period. In order to qualify as an air sanitizer under these test conditions a reduction of airborne bacteria on the order of 90% or better (compared to the control) must be obtained after treatment.

That is, if the relative number of colonies obtained per cubic foot of inoculated air is substantially reduced, i.e., by at least about 90%, the composition is qualified as an air sanitizer. This reduction in colonies is based on a subjective comparison of the untreated control air volume (15 cubic feet) which comprises one quarter of the agar surface and which represents the standard air contaminant load of each specific test, with the treated air volume. The latter comprises three-quarters of the agar surface. Thus, each petri dish comprises a control portion and a test portion. The results obtained lend themselves to photographing and it has been found helpful to photograph the various petri dishes under the same lighting conditions, shutter speed, etc. after the incubation period.

For the purposes of the present invention, the results are classified as S (satisfactory, i.e., over 90% effective), M (marginal, i.e., about 90% effective), and U (unsatisfactory, i.e., significantly below 90% effective).

The following examples are given by way of illustration only and to provide further understanding of the invention. These examples are not intended as limitations of this invention, many apparent variations of which are possible without departing from the spirit and scope thereof. All percentages are by weight unless otherwise indicated.

Example 1

An intermediate composition containing the active ingredients is prepared by dissolving the following substances in about 83.41% anhydrous ethanol:

(1) About 0.175% of a mixture of Formula II(a) and III(a) quaternaries in a ratio of about 1:1,
(2) About 0.20% of the Formula V surfactant,
(3) About 15.175% water, and
(4) About 1.04% perfume, corrosion inhibitor, and masking agents.

The intermediate is introduced into a pressure package and comprises about 75% by weight of the contents. The propellant dichlorodifluoromethane is introduced into the package at a concentration of about 25% and the package is then hermetically sealed.

This composition has an internal pressure of about 54–56 p.s.i.g. at 21° C., is stable for prolonged periods

under various conditions, and comprises a gaseous phase and a homogeneous liquid phase. This composition can be discharged without agitating and when conventional valving such as described above is employed, the composition can be essentially completely discharged while producing a substantially constant spray pattern with a constant composition.

Examples 2–14

The effect of varying the concentration of certain components of the composition described in Example 1 on the surface disinfectant-air sanitizing activity is illustrated in Table 1 below.

TABLE I

Ex.	Water, percent	Ethanol, percent	Formulas II(a) and III(a) [1]	CCl_2F_2 percent	Test Results: Surface Disinfecting *S. Aureus*	Test Results: Surface Disinfecting *S. Choleraesuis*	Test Results: Air Sanitizing
2	.55	53.58	.096	[3] 45	10+	[2]	S to M.
2a	1.48	56.50	.103	[2] 41	9+	10+	[2].
3	3.25	60.72	.114	[3] 35	10+	[2]	S to M.
4	5.18	62.73	.121	[3] 31	7+	[2]	[2].
5	7.50	66.31	.131	25	2+	0+	M to U.
6	11.25	62.56	.131	25	0+	0+	S.
7	11.25	62.67	.075	25	0+	0+	M.
8	11.25	62.71	.056	25	0+	0+	[2].
9	11.25	62.75	.038	25	1+	3+	U.
10	7.50	41.71	.088	50	0+	1+	S.
11	9.75	54.22	.114	35	1+	0+	[2].
12	12.00	66.73	.140	20	0+	0+	[2].
13	12.75	70.89	.149	15	0+	0+	M to U.
14	13.50	75.07	.158	10	1+	1+	M to U.

The concentration of surfactant, perfume and corrosion inhibitor was maintained essentially constant in all compositions.

[1] Formulas II(a) and III(a) are in a 1:1 ratio

[2] Not tested.

[3] Propellant concentration increased to provide uniform internal pressure of between about 54–58 p.s.i. at 21° C. to assure uniform spray pattern.

S=Satisfactory. M=Marginal. U=Unsatisfactory.

It is evident from Examples 2 through 5 above that concentrations of water up to 7.5% fail to provide satisfactory surface disinfecting. In these examples the difference in the water present was made up by adding additional appropriate amounts of ethanol. It has been observed that such additions would not significantly effect the germicidal activity of the composition, and, therefore, a substantially true indication of the effect of water concentration is obtained. It should be noted that the concentration of CCl_2F_2 was increased to provide a suitable vapor pressure and a satisfactory spray.

The effect of varying the concentration of the Formula II/III quaternaries is shown in Examples 2 through 14. It is evident that the air sanitizing activity and surface disinfecting activity of the composition containing 0.038% quaternaries would be unsatisfactory.

The effect of varying the concentration of propellant is illustrated in Examples 10 through 14. It is evident that concentrations of CCl_2F_2 of 50% and 35% produce unsatisfactory surface disinfecting activity. However, the air sanitizing activity Example 10 was satisfactory. At lower concentrations, i.e. 10% propellant, unsatisfactory surface disinfecting and marginal air sanitizing activity is obtained. In addition, as a result of increasing the propellant concentration the concentration of the Formula II and III quaternaries is correspondingly reduced, i.e., at 50% CCl_2F_2, the quaternary concentration is reduced to .088.

Example 15

The composition described in Example 1 was modified to show the effect of having no water and no Formula II and III quaternaries present.

Example 16

A composition of the invention similar to Example 5 was prepared containing the following:

Ingredient:	Percent
Ethanol	62.56
Water	11.25
Formula II(a)/III(a) quaternary in a 1:1 ratio	0.13
Formula V surfactant	0.15
CCl_2F_2 propellant	25.00
Perfume/corrosion inhibitors masking aids	0.91
	100.00

A similar composition was prepared except that 0.15% by weight of a nonyl ethylene oxide adduct surfactant was substituted for the Formula V surfactant. (This compound contained 6 moles of ethylene oxide per mole of nonyl phenol and is recognized as an outstanding surfactant and wetting agent.)

These compositions are packaged in conventional pressure packages which are lined with an epoxy-phenolic resin. The packages are filled to about 10% by volume headspace. After storage for 30 days at 38° C. representative samples of containers containing each of the compositions are selected at random and opened to check the containers' liners for corrosion.

The general corrosion observations are set forth in Table 2 below:

TABLE 2

Portion of Container	Formula V Surfactant	Nonyl phenol/ethylene oxide
Body	Very slight pin-point detinning under protective coating.	Spot rusting throughout with pits in the steel of the container.
Bottoms	Liner bleached	Surface rust apparent.
Tops	Satisfactory	Considerable rust at seam between body wall and top.

It is evident from the above observations that compared to the nonyl phenol ethylene oxide adduct surfactant the Formula V surfactant provides unexpected corrosion resistance to the compositions of the invention.

Examples 17–21

Set forth in Table 3 below are further examples illustrative of compositions of the invention.

TABLE 3

Ex. No.	Ethanol, Percent	Water, Percent	Formula II		Formula III		Ratio of Formula II: Formula III	Percent Formula II/III	M
			Quat. R_1 n-alkyl	Percent	Quat. R_2 n-alkyl	Percent			
17	50	25	C_{14}	55	C_{12}	45	1:2	0.05	Na
			C_{16}	35	C_{14}	35			
			C_{12}	2	C_{16}	12			
			C_{18}	8	C_{18}	8			
18	70	10	C_{14}	65	C_{12}	55	2:1	0.8	K
			C_{16}	25	C_{14}	25			
			C_{12}	8	C_{16}	19			
			C_{18}	2	C_{18}	1			
19	60	15	C_{14}	60	C_{12}	50	1:1	0.13	Na
			C_{16}	30	C_{14}	30			
			C_{18}	5	C_{16}	17			
			C_{12}	5	C_{18}	3			
20	55	20	C_{14}	58	C_{12}	51	1:1.5	0.10	H
			C_{16}	32	C_{14}	30			
			C_{18}	6	C_{16}	11			
			C_{12}	4	C_{18}	8			
21	65	12	C_{14}	56	C_{12}	48	1:1	0.5	H
			C_{16}	30	C_{14}	27			
			C_{18}	6	C_{16}	22			
			C_{12}	8	C_{18}	3			

Ex. No.	Formula IV Surfactant		Percent Formula IV	Propellant	
	R_3	R_4		Type	Percent
17	Hydrocarbon radical having 4 carbon atoms.	Aliphatic hydrocarbon group having 4 carbon atoms.	0.05	CCl_2F_2	24.9
18	Hydrocarbon radical having 18 carbon atoms.	Hydroxy substituted hydrocarbon group having 4 carbon atoms.	1.0	CCl_2F_2	18.2
19	Hydrocarbon radical having 11 carbon atoms.	Aliphatic hydrocarbon group having 2 carbon atoms.	0.15	CCl_2F_2	24.72
20	Hydrocarbon radical having 14 carbon atoms.	50:50 mixture of aliphatic ether groups having 3 carbon atoms and aliphatic hydroxy substituted ether groups having 3 carbon atoms.	0.5	50:50 mixture CCl_2F_2 and CCl_3F.	24.4
21	Hydrocarbon radical having 16 carbon atoms.	50:50 mixture of aliphatic keto groups containing 14 carbon atoms and aliphatic hydroxy substituted keto groups having 4 carbon atoms.	0.75	50:50 mixture of CCl_2F_2 and $C_2Cl_3F_3$.	21.75

While this invention has been described and exemplified in terms of its preferred embodiments, those skilled in the art will appreciate that variations can be made without departing from the spirit and scope of the invention.

It is claimed:

1. A two phase, pressurized surface disinfectant-air sanitizing composition comprising a gaseous phase and a stable homogeneous liquid phase wherein said liquid phase contains:

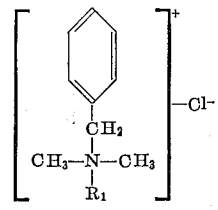
(a) at least about 10% by weight water,

(b) at least about 15% by weight of a normally gaseous halogenated hydrocarbon propellant,

(c) ethanol in a concentration sufficient to form a homogeneous solution with said water and propellant,

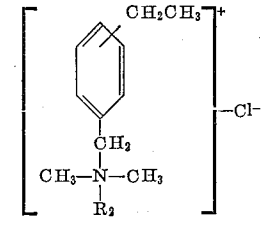
(d) at least about 0.050% by weight of a mixure of quaternaries comprising:

(1) compounds represented by the structural formula:



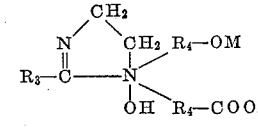
wherein R_1 represents a mixture of n-alkyl groups comprising from about 55% to about 65% C_{14}, from about 25% to about 35% C_{16}, from about 2% to about 8% C_{12}, and from about 2% to about 8% C_{18}, and

(2) compounds represented by the structural formula:



wherein R_2 represents a mixture of n-alkyl groups comprising from about 45% to about 55% C_{12}, from about 25% to about 35% C_{14}, from about 12% to about 22% C_{16}, and from about 1% to about 8% C_{18} alkyl groups, and

(e) an amphoteric surfactant in a concentration from about 0.05% to about 1.0% by weight, represented by the structural formula:



wherein R_3 represents a hydrocarbon radical having from about 4 to about 18 carbon atoms, R_4 is selected from the group of aliphatic hydrocarbon and oxygenated aliphatic hydrocarbon groups consisting of:

(1) aliphatic hydrocarbon groups having from 1 to 4 carbon atoms,

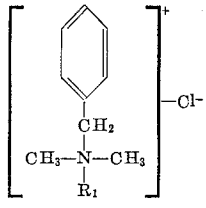
(2) hydroxy substituted hydrocarbon groups having from 1 to 4 carbon atoms,

(3) aliphatic ether groups, having from 2 to 4 carbon atoms with each of said groups having a single ether linkage therein,
(4) aliphatic hydroxy substituted ether groups having from 2 to 4 carbon atoms,
(5) aliphatic keto groups containing from 2 to 4 carbon atoms, and
(6) aliphatic hydroxy substituted keto groups having from 2 to 4 carbon atoms, and

M is selected from the group consisting of potassium, sodium, and hydrogen.

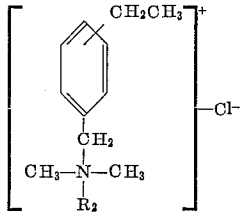
2. A composition according to claim **1** wherein the mixture of quaternaries comprises:

(1) compounds represented by the structural formula



wherein R_1 represents a mixture of n-alkyl groups comprising about 60% by weight C_{14}, about 30% by weight C_{16}, about 5% by weight C_{12}, and about 5% by weight C_{18}, and

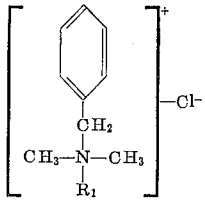
(2) compounds represented by the structural formula:



wherein R_2 represents a mixture of n-alkyl groups comprising about 50% by weight C_{12}, about 30% by weight C_{14}, about 17% by weight C_{16}, and about 3% by weight C_{18}.

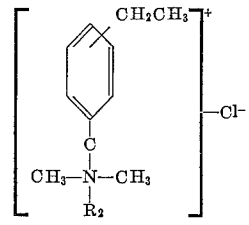
3. A package of self-propelling liquid composition comprising a fluid-tight container having a valve assembly for discharging the contents wherein the contents comprise a stable homogeneous liquid phase which is confined in the container under a vapor pressure provided by a gaseous phase, said liquid comprising:

(a) at least about 10% by weight water,
(b) at least about 15% by weight of a normally gaseous halogenated hydrocarbon propellant,
(c) ethanol in a concentration sufficient to form a homogeneous solution with said water and propellant,
(d) at least about 0.050% by weight of a mixture of quaternaries comprising:
(1) compounds represented by the structural formula:



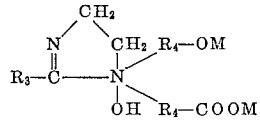
wherein R_1 represents a mixture of n-alkyl groups comprising from about 55% to about 65% C_{14}, from about 25% to about 35% C_{16}, from about 2% to about 8% C_{12}, and from about 2% to about 8% C_{18}, and

(2) compounds represented by the structural formula:



wherein R_2 represents a mixture of n-alkyl groups comprising from about 45% to about 55% C_{12}, from about 25% to about 35% C_{14}, from about 12% to about 22% C_{16}, and from about 1% to about 8% C_{18} alkyl groups, and

(e) an amphoteric surfactant in a concentration from about 0.05% to about 1.0% by weight, represented by the structural formula:



wherein R_3 represents a hydrocarbon radical having from about 4 to about 18 carbon atoms, R_4 is selected from the group of aliphatic hydrocarbon and oxygenated aliphatic hydrocarbon groups consisting of:

(1) aliphatic hydrocarbon groups having from 1 4 carbon atoms,
(2) hydroxy substituted hydrocarbon groups having from 1 to 4 carbon atoms,
(3) aliphatic ether groups, having from 2 to 4 carbon atoms with each of said groups having a single ether linkage therein,
(4) aliphatic hydroxy substituted ether groups having from 2 to 4 carbon atoms,
(5) aliphatic keto groups containing from 2 to 4 carbon atoms, and
(6) aliphatic hydroxy substituted keto groups having from 2 to 4 carbon atoms, and

M is selected from the group consisting of potassium, sodium, and hydrogen.

4. A composition according to claim **1** wherein the concentration of water comprises from about 10% to about 25% by weight of the liquid phase.

5. A composition according to claim **1** wherein the normally gaseous halogenated hydrocarbon propellant has the structural formula:

$$C_nH_xCl_yF_z$$

wherein n is a whole number from 1 to 2, x is a whole number from 0 to 4, y is a whole number from 0 to 3, and z is a whole number from 1 to 4, and the sum of x, y, and z is equal to $2n+2$ with the proviso that when n equals 1, y is at least 1.

6. A composition according to claim **5** wherein the propellant comprises from at least about 15% by weight to about 30% by weight of the liquid phase.

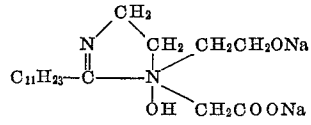
7. A composition according to claim **1** wherein ethanol comprises from about 50% to about 70% by weight of the liquid phase.

8. A composition according to claim **1** wherein the mixture of quaternaries described in subparagraphs (1) and (2) are in a ratio from about 1:2 to 2:1 respectively.

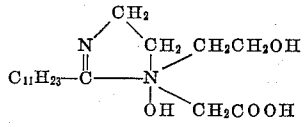
9. A composition according to claim **8** wherein said ratio is about 1:1.

10. A composition according to claim **1** wherein the concentration of quaternary mixtures comprises from about 0.050% by weight to about 0.800% by weight of the liquid phase.

11. A composition according to claim 1 wherein the amphoteric surfacant has the structural formula:



12. A composition according to claim 1 wherein the amphoteric surfactant has the structural formula:



13. A method of disinfecting surfaces and sanitizing the air in enclosed spaces comprising discharging the composition of claim 1 onto contaminated surfaces and into the air in enclosed spaces.

14. A composition according to claim 1 wherein the propellant is dichlorodifluoromethane.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,282,776 November 1, 1966

Eugene D. Kitzke et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 13, TABLE I, fifth column, line 2 thereof, for "$^{2}41$" read -- $^{3}41$ --; column 18, lines 5 to 16, for the portion of the formula reading



read



same column 18, lines 33 and 34, for "from 1 4" read -- from 1 to 4 --.

Signed and sealed this 5th day of September 1967.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents