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2,727,007

DETERGENT-GERMICIDE COMPOSITION

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The present invention is directed to germicidal compositions, more particularly to combinations of germicides with detergents and particularly adapted for use in the food industries.

It has been known for some time that quaternary ammonium compounds having germicidal properties are effective against certain pathogenic bacteria. However, such compounds have been found ineffective for many applications because of the presence in natural waters of small amounts of compounds of ferric iron, calcium, magnesium and the like which seem to inactivate the germicide. It has also been found that such germicides are less effective against Gram negative bacteria than against Gram positive bacteria, which has greatly limited the usefulness thereof. Attempts have been made to overcome these difficulties by adding to a solution containing such germicides an alkaline salt in sufficient quantity to raise the pH above 9.0. However, this caused an undesirable result in that the calcium and magnesium ions formed an objectionable precipitate. In an attempt to prevent such precipitation, a small amount of a polyphosphate was added but this had a further disadvantage in that such addition caused the precipitation of the germicide itself. In certain compositions tetra sodium pyrophosphate was used to prevent precipitation of the calcium and magnesium compounds but it was relatively ineffective although it did minimize to a certain extent the precipitation of the germicide.

There were other disadvantages in the use of said quaternary ammonium germicides together with detergents in the sanitizing of food processing machinery in that a relatively large amount of the germicide was necessary in order to give adequate germicidal action. Because of the expense of such germicides, it became commercially impossible to use in many cases. Also, this type of germicide acts as an anti-detergent agent, causing flocculation of the dirt and counteracting the detergent action of the various detergents used. Also, these germicides were relatively ineffective against the Gram negative bacteria.

The present invention is intended and adapted to overcome the difficulties and disadvantages inherent in compositions of the type described, it being among the objects of the present invention to provide a quaternary ammonium germicidal and detergent composition wherein the activity of the germicide is substantially increased.

It is also among the objects of the present invention to provide a composition of the type described, which is highly effective against Gram negative as well as Gram positive bacteria.

It is further among the objects of the present invention to provide a composition having increased detergency and having a high degree of water softening effects.

It is still further among the objects of the present invention to provide a composition which may be used to clean and sanitize food processing machinery to combat pathogenic organisms, and which is highly economical in such use.

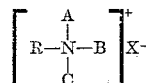
It has now been discovered by extensive experimenta-

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tion that quaternary ammonium germicides may be activated so that their potency is increased from two to five times its previous value. This is accomplished by providing an environment in the form of other chemical substances so that the germicide becomes relatively insensitive to the salts in the water used. As a result, the germicides become equally effective against the Gram negative bacteria and they may be used at a much lower concentration than previously, greatly decreasing the cost of the composition. The invention also lowers the concentration of the germicide, which minimizes and substantially eliminates the anti-detergent action of the cation of the germicides.

In practicing the present invention, it has been found that an ideal ionic environment is provided by introducing into the composition containing said germicide, a mixture of an alkali metal carbonate and an alkali metal polyphosphate. The ratio of said two constituents is 1 part of the alkali metal carbonate to 2-7 parts of the polyphosphate. Within these ratios it has been found that excellent results are obtained by utilizing a ratio of 1 part of said carbonate to 4-5.5 parts by weight of the polyphosphate. Optimum results may be obtained when certain of the higher polyphosphates are used, namely, those containing at least 3 atoms of phosphorus in the molecule. The amount of the quaternary ammonium germicide used in the compositions is preferably from 1% to 8% of the complete composition.

The germicide is one which has been known for a number of years and has been found effective for medicinal purposes, and having the following structural formula.



and having germicidal properties, and in which A, B and C represent H, alkyl, aryl and heterocyclic groups, R represents lipophilic long chain alkyl, polycyclic and aryl-alkyl group, and X represents the negative radical of an acid.

The compositions coming within the scope of the present invention usually have the following proportions:

	Percent by weight
Quaternary NH_4 Compound	1-8
Alkali metal polyphosphate	20-75
Alkali metal carbonate	10-25
Non-ionic wetting agent	1-10

The presence of a non-ionic wetting agent has been found to be highly advantageous in promoting the detergent effect of the composition without interfering with the germicidal value thereof. There may be added to the composition substantial amounts of other detergent salts of inorganic acids. From 1% to 50% of such added salts may be used, thereby giving a better detergency or a higher pH for a particular purpose. The wetting agents may be of various types but must be non-ionic or cationic in character. Among such compounds are the polyalkylene glycol ethers and esters thereof, as well as condensation products of alkylolamines and higher fatty acids.

The following are specific examples of compositions made in accordance with the present invention:

Example 1

The following composition was made:

	Percent
Sodium tripolyphosphate	75
Sodium carbonate	15
Polyethyleneglycol ether	4
Quaternary NH_4 germicide (50% H_2O)	6

This composition has been found highly effective for

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general detergency in the care of food processing machinery.

Example 2

The following composition was made:

	Percent
Sodium tetrapolyphosphate.....	50
Sodium carbonate.....	10
Polyethyleneglycol ether.....	4
Quaternary NH ₄ germicide.....	3
Trisodium phosphate.....	33

This composition has proven highly effective in the care of food processing machinery which is hard to clean.

Example 3

A comparative test was made between applicants' composition and a prior art composition in order to determine the relative effectiveness thereof. The prior art composition had the following formula:

	Percent
Sodium metasilicate.....	30
Tetrasodium pyrophosphate.....	55
Quaternary NH ₄ germicide.....	10
Polyethyleneglycol ether.....	5

Applicants' formula was that given in Example 1. The compositions were tested under identical conditions against *E. coli*, with the following results:

	Bacteria Surviving after 2 Minutes			
	Applicants' Formula		Prior Art Formula	
	No Milk	2% Skim Milk	No Milk	2% Skim Milk
<i>E. coli</i>				
Distilled water.....	0	0	0	1,710
5 p. p. m. Ferrie Iron.....	0	0	5	1,845
10 grain Hardness.....	0	115	0	18,800
20 grain Hardness.....	0	155	5	TNC
30 grain Hardness.....	0	2,795	13,750	TNC

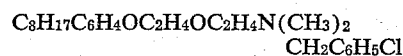
It will be noted that using applicants' formula in various types of water, from distilled water to hard water, there was no survival of bacteria. On the other hand, with the prior art formula, in hard water there was a very large growth of bacteria. When the two types of compositions were tested in skim milk, applicants' formula showed a very modest growth of bacteria, but only in the hard water. On the other hand the prior art formula showed a growth of bacteria even in distilled water and in water of low hardness, permitting a substantial growth of bacteria, and the harder the water the more prolific was the growth so that in the moderate and hard waters the bacteria were too numerous to count. In the compositions the same germicide was used and the same wetting agent. The germicide in both compositions was in a concentration of .3% in water. The number of bacteria listed in the table are per cc.

The various non-ionic wetting agents include the fatty acid esters or ethers of higher polyalcohols such as the alkylene glycols having 2 to 4 carbon atoms in each alkylene group. The molecular weight of the polyalcohols is at least 200 and preferably 400 or more. The fatty acids combined in the compositions have from 12 to 22 carbon atoms. The non-ionic condensation products are made with fatty acids having from 12 to 22 carbon atoms and with alkylolamines in which the alkyl group contains from 2 to 4 carbon atoms. The alkylolamine contains 2 or 3 alkyl groups and the ratio of fatty acids to the alkylolamine is usually 1 mol. to 1-2 mols. of said amine.

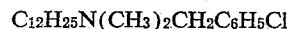
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The following are specific examples of the quaternary ammonium compounds suitable for the purpose:

Di-isobutyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride



Dodecyl dimethyl benzyl ammonium chloride (50% aqueous solution)



Dodecyl benzene trimethyl ammonium chloride (50% aqueous solution)

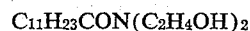


The following examples illustrate the wetting agents which may be employed in the present compositions:

Polyglycol ether

$\text{C}_6\text{H}_5(\text{CH}_2)_9\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$

Ninol type detergent (fatty acid-amino condensate)



Polyethylene glycol monolaurate

$\text{C}_{11}\text{H}_{23}\text{COOC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OH}$

In the presence of the ionic media in the above compositions, a product containing 2 to 4% of the quaternary ammonium germicide and used at a concentration of 0.30% in aqueous solution provides solutions containing 60 to 120 p. p. m. of said germicide. Such solutions give superior germicidal action than those compositions containing 150 to 200 p. p. m. but without the ionic media of the present invention. Furthermore, the detergency and water softening properties of the new compositions are distinctly superior to those of prior types of compositions, and the superiority is evidenced by the absence of scale, scum and film on the articles cleaned thereby.

The present compositions are eminently suitable for use on dairy farms for treatment of utensils and equipment. They are effective not only against gram positive but also particularly against gram negative bacteria. They are effective in combatting thermophilic organisms, namely, those withstanding high temperatures. They are suitable for use in plants which process dairy products in the control of all types of bacterial contamination, especially *E. coli* and other Gram negative types. They are useful in canneries and other food processing plants in controlling the flat sour type of spoilage caused by thermophilic and by spore forming bacteria, such as *B. subtilis*.

Although the invention has been described setting forth several specific embodiments thereof, the invention is not limited thereto as they were inserted for the purpose of illustration of the character of the invention. Various changes in the details may be made within the scope thereof. For instance, the compositions may be used under other conditions of temperature and concentration than described above. The ratio of the constituents may be altered and equivalent materials may be substituted in whole or in part. To the compositions may be added other substances which do not interfere with the functioning thereof. The trisodium phosphate may be replaced in whole or in part by sodium metasilicate, boraz, or other alkaline detergents; mono- or dialkali metal phosphates may be used. The sodium carbonate may be formed in the final solution and may be replaced in the composition by equivalent amounts of mixtures of such substances as alkali metal silicates and bicarbonates which react to give the carbonates.

These and other changes may be made in the details without departing from the spirit of the invention, which is to be broadly construed and not to be limited except by the character of the claims appended hereto.

We claim:

1. A detergent-germicide composition consisting of a quaternary ammonium germicide, an alkali metal carbonate and an alkali metal polyphosphate taken from the class consisting of alkali metal triphosphates and tetraphosphates, the ratio of carbonate to polyphosphate being 1 to 4-5.5.

2. A detergent-germicide composition consisting of a quaternary ammonium germicide, an alkali metal carbonate and an alkali metal polyphosphate taken from the class consisting of alkali metal triphosphates and tetraphosphates, the ratio of carbonate to polyphosphate being 1 to 2-7, the amount of said germicide being 2 to 4% by weight of said composition.

3. A detergent-germicide composition consisting of a quaternary ammonium germicide, an alkali metal carbonate and sodium tripolyphosphate, the ratio of carbonate to polyphosphate being 1 to 2-7.

4. A detergent-germicide composition consisting of a quaternary ammonium germicide, an alkali metal carbonate and sodium tetrapolyphosphate, the ratio of carbonate to polyphosphate being 1 to 2-7.

5. A detergent-germicide composition consisting of a quaternary ammonium germicide, an alkali metal carbonate and an alkali metal polyphosphate taken from the class consisting of alkali metal triphosphates and tetraphosphates, the ratio of carbonate to polyphosphate being 1 to 2-7, and containing a substantial amount of an inorganic salt having detergent properties.

6. A detergent-germicide composition consisting of a quaternary ammonium germicide, an alkali metal carbonate and an alkali metal polyphosphate taken from the class consisting of alkali metal triphosphates and tetraphosphates, the ratio of carbonate to polyphosphate being 1 to 2-7, and containing 1 to 50% by weight of an inorganic salt having detergent properties.

7. A detergent-germicide composition consisting of a quaternary ammonium germicide, an alkali metal carbonate and an alkali metal polyphosphate taken from the class consisting of alkali metal triphosphates and tetraphosphates, the ratio of carbonate to polyphosphate being 1 to 2-7, and containing a substantial amount of an alkali metal salt taken from the class consisting of phosphate, metasilicate and borate having detergent properties.

8. A detergent-germicide composition consisting of a quaternary ammonium germicide, an alkali metal carbonate and an alkali metal polyphosphate taken from the class consisting of alkali metal triphosphates and tetraphosphates, the ratio of carbonate to polyphosphate being 1 to 2-7, and containing a substantial amount of a non-ionic wetting agent.

9. A detergent-germicide composition consisting of a quaternary ammonium germicide, an alkali metal carbonate and an alkali metal polyphosphate taken from the class consisting of alkali metal triphosphates and tetraphosphates, the ratio of carbonate to polyphosphate being 1 to 2-7, and containing a substantial amount of a non-ionic wetting agent taken from the class consisting of fatty acid esters and ethers of higher polyalcohols and condensation products of higher fatty acids and polyalkylolamines.

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